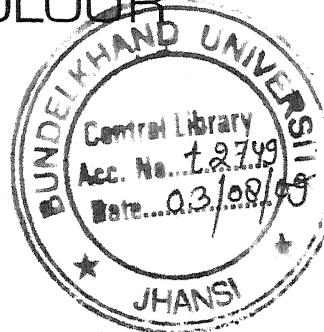


PHYSICO-CHEMICAL STUDIES OF ASYMMETRIC PHTHALEINS - THEIR SYNTHESIS AND COLOUR



THESIS

Submitted in fulfilment of requirements of
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Research Supervisor :

Dr. I. M. Beg
D. Phil.

Research Scholar :

Ms. Deepti Gupta
M.Sc.

Department of Chemistry
Dayanand Vedic Post Graduate College, Orai - 285001 (U.P.)

Department of Chemistry
D.V. Postgraduate College, Orai-285 001 (U.P.)

Dr I. M. Beg, D.Phil.

Head of Department

Certificate

I am pleased to certify that the work presented in this thesis entitled, "PHYSICO-CHEMICAL STUDIES OF ASYMMETRIC PHTHALEINS - THEIR SYNTHESIS AND COLOUR" was carried out under my supervision by the candidate Ms Deepti Gupta solely by herself for the degree of DOCTOR OF PHILOSOPHY of BUNDELKHAND UNIVERSITY. I further certify that the work and the approach adopted by her is entirely original and it has neither been carried out by anyone else in the same form or manner nor it has been submitted for any other degree of this or any other University.

Ms Deepti has put in more than two hundred days of work in the Chemical Laboratory of Dayanand Vedic Postgraduate College, Orai

Orai

Dated 24/12/06

(DR I.M. BEG)

*Department of Chemistry
Dayanand Vedic Postgraduate College,*

Orai

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Orai

Dated 24-12-04

Deepti Gupta
DEEPTI GUPTA, M.Sc.

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CHAPTER

ONE

**INTRODUCTION
GENERAL SURVEY
AND THEORETICAL CONSIDERATIONS**

INTRODUCTION, GENERAL SURVEY AND THEORETICAL

CONSIDERATIONS

PREAMBLE

Among the charming variety of things that fulfil our universe, colour occupies the pride of place. The man, since the advent of civilization, has always enjoyed colour. He has ever since tried to duplicate the colours of nature and has exploited them in a number of ways. Ancients used coloured substances of natural origin to decorate their skin, fabrics and other materials. However, the choice was limited. It was only in the nineteenth century that man succeeded in synthesizing the colouring substance in the Chemist's laboratory. Today, the colourants having every colour of the rainbow and their various hues and shades have been synthesized. In many cases, he has improved over nature and given mankind many new substances with colours and shades that are far more superior and better in all respects.

1.1 THE HISTORY OF COLOURANTS:

Even though its appeal has especially been cognate to human taste and liking, colour has increasingly been called upon to sell products and so vast industries are now dependent upon the availability of artificial colourants. Clothing's, carpets, wall paints, plastic veneers, colour photographs, medicine, food and what not, all contain colouring substances. Throughout the history of man, dyes and pigments, both natural and artificial, have been important articles of commerce. Consequently, considerable interest has been shown in the theoretical and empirical evaluation of relationship between their colour and their molecular structure. The widening areas into which the colours now intrude have accentuated this interest. In fact, colour - structure relationships are now of value to the scientists working in many seemingly unrelated disciplines. Apart from

business and industry, dyes and pigments enjoy their applications in science², biology³, medicine⁴⁻³¹, engineering, architecture and technology³²⁻³⁴, art, philosophy and psychology³⁵ and above all modern living as we see every day³⁴. Liquid crystal systems, high-energy radiation sensors and a number of organic dye lasers³⁶⁻⁴⁰ are recent examples of varied uses of synthetic colouring matters. But the burden to meet the ever-increasing demand of artificial colourants consequent upon a bewildering range of their applications has given no respite to the humble organic chemist who has been working relentlessly to cater to the demands of our times.

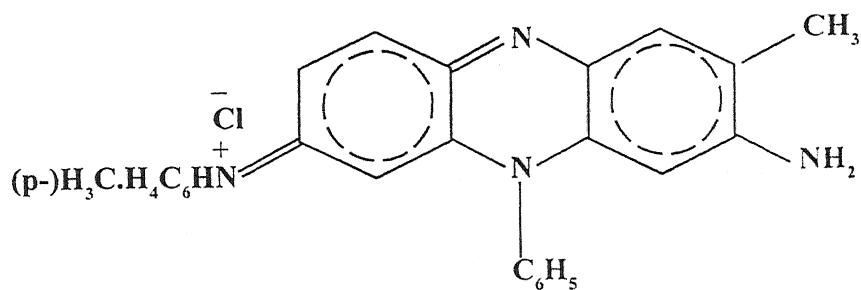
1.1.1 NATURAL COLOURANTS:

Previously in their inception the materials used to produce colours were few in numbers and were obtained from vegetable sources. The three most prized colours were the blue indigo, the red madder and the yellow of the saffron. Other colouring matters were of animal origin. 'Tyran Purple' obtained from a small snail 'Murex Bandaris' found near Tyre was so expensive that it was available only to those of high status. Hence its name ' Royal Purple'. Then there was 'Cochineal' obtained from the dried body of female insects, 'Caecus cacti'. During those times only such type of materials constituted the colouring or the dyeing material.

1.1.2 MAN-MADE COLOURANTS:

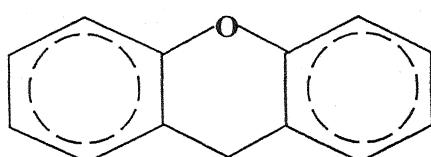
The ingenuous colourants could not meet the demands in terms of quality and quantity and this circumstance encouraged the early search of synthetic dyes with superior properties and availability in plenty. However, only a few additions could be made to the existing natural colourants until the rise of the modern synthetic dye industry⁴¹ in late nineteenth century.

Scholarly research due to Perkin⁴² and the vigorous efforts by such leading organic



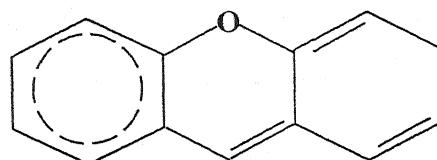
MAUVEIN

FIGURE 1.01



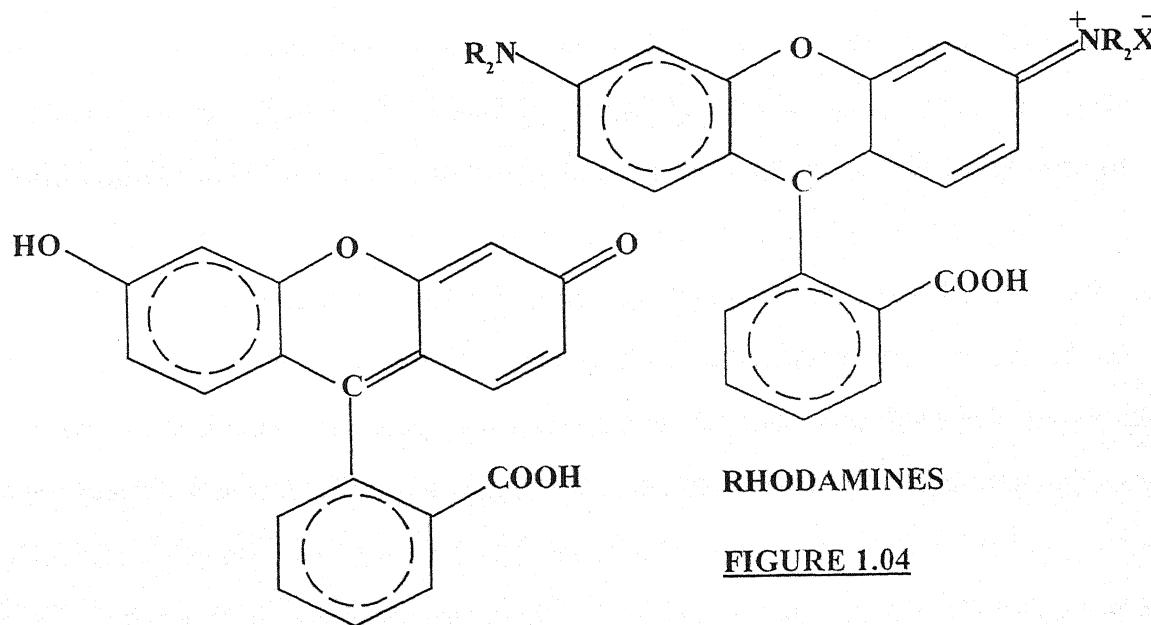
XANTHEN

FIGURE 1.02



3H-ISOXANTHEN

FIGURE 1.03



RHODAMINES

FIGURE 1.04

FLUORESCIN
QUINONOID FORM

FIGURE 1.05

chemists as Hoffman, Baeyer, Caro, Griess, Graebe, Liebermann, Otto Fischer, Emil Fischer, Nietzki⁴³ and a host of others are responsible for the initiation of the modern multibillion dollar synthetic dye-stuff industry. Later, however, research chemists were more closely concerned with industry largely carried out the development of new organic dyes. Some of them are Sandmeyer, Heumann, Schmidt, Green⁴⁴ etc.

PICRIC ACID was the first man-made dye prepared by Woulfe in 1771 by of the action of nitric acid on natural Indigo. IN 1885 a technical method was introduced to prepare it from coal tar. The first coal tar dye reported by Ferdinand Runge in 1834 was AURIN, the ROSOLIC ACID. It along with usual mordents produced the red colours and lakes that rivaled those produced from natural dyes cochineal and alizarin. Yet neither of these compounds was manufactured on a commercial scale. The unreliability of supply and the heavy cost was the cause. That, for the little knowledge about the components of coal tar and that for Kekule's theory of structure of benzene was not proposed until 1865, Ringe's experiments could not be expansive.

In 1843, Hoffman had observed that aniline prepared at the time gave red colours under certain conditions. In 1856, Perkin⁴⁵ oxidized aniline sulphate with potassium dichromate and obtained a purple dye called MAUVE. Mauvine or aniline purple was the first dye to be manufactured commercially. It was the sensation of 1862 World Exhibition in London. The first coal tar dye caught on and the race for new dyes and colours began in right earnest. From a waste product the coal tar was transformed into a commodity of immense use. Synthesis of Martius Yellow, Caro's Induline Blue and Hoffman's violet followed quickly and was accepted widely. The discovery that the colouring matter could be prepared by oxidation of aniline lead to the study of behaviour of this base towards various oxidizing agents. Soon, thereafter, the bright red dye FUCHSIN was prepared in 1859 by Verguin in Lyons, France, by the oxidation of aniline by tin chloride, which made an even greater impact than the MAUVE. After Hoffman showed that FUCHSIN is a derivative

of triphenylmethane, this class of dyes was investigated extensively and came into use on a large scale.

The discovery of early man-made aniline dyes was necessarily the result of intuitive following of clues derived from experiments only since the constitution of even benzene was unknown. In the year 1865 Kekule published his theory of the structure of benzene and thus paved the way for elucidation of the structure of aromatic organic compounds and for the development of the dye industry on a rational basis. The artificial dyes, although more brilliant, were less permanent than the natural dyes. Chemists began investigations on the structure of natural products to establish their structures ⁴⁶⁻⁵⁰.

The structure of popular red dye from the root of madder, alizarin was quickly determined in 1868 by Carl Graebe and Carl Liebermann⁵¹. It was found to be a derivative of anthracene. Benzene, naphthalene and anthracene are colourless products of coal tar distillation. By simple chemical addition of chromophoric groups ⁵², beautiful dyes can be created. This finding in the nineteenth century excited the fashion world to colourful fantasies. Graebe and Liebermann⁵³ in 1868 afforded the synthesis of alizarin. In 1869, Graebe, Liebermann and Perkin were able to achieve its commercial production. This followed the manufacture of a family of alizarin like dyes with different colours. In 1871, Baeyer prepared FLUORESCEIN and in the same year Caro prepared Eosine after the start of commercial production of resorcinol. While the attention of the chemists was directed towards the synthesis of alizarin, another class of dyestuffs, the azo dyestuffs, appeared in the market in 1876. Griess had already synthesised azo compounds in 1862 and one member of the group. BISMARK BROWN had already been prepared on the commercial scale since 1863. In 1875, Caro discovered CHRYSOIDINE and indicated the technical value of the Griess method of preparing the azo compounds. When azo dyestuffs were first introduced, it was considered that only orange and yellow colours could be obtained in this series. This idea was dispelled by the discovery of FAST RED A by Caro in 1878. Thus we see that

Heinrich Caro⁵⁴ contributed much to the synthetic dye industry and must be remembered as such.

In 1879, the oldest known colouring matter Indigo was synthesized by Baeyer and was put to commerce in 1880. However, Karl Heumann⁵⁵ achieved successful industrial production of synthetic Indigo in 1890. Baeyer's Indigo synthesis marked the beginning of the chemical industry and led to the development of organic chemistry whose economic strength was then recognized. Thus was born the chemical industry⁵⁶.

Since then the progress in the field of dyes has been very rapid⁵⁷⁻⁸⁵, here is a list of new milestones: Direct dyes from azo compounds for cotton were introduced in 1880; sulphur colours from coal tar derivatives in 1893; anthraquinone dyes, vat dyes in 1901; azoic dyes or ice colours in 1911; acetoanilides in 1923; phthalocyanines in 1934; fluorescent brightening agents in 1940 and fibre reactive procion dyes in 1956. Thus natural dyestuffs were almost completely displaced by synthetic colourants. Fundamental research on new dyes is constantly in progress⁸⁶⁻¹⁰⁰ and synthetic dyes are dominating the field now. Today the dye industry occupies an important place among the major chemical industries.

1.2 DYESTUFFS AND PIGMENTS

1.2.1 DEFINITION

An organic compound that may be used to impart colour to a substance is called a dyestuff. It may be used for the colouring of animal, vegetable or synthetic fibres and similar products such as wool, cotton, silk, linen, rayon, fur, leather, paper, nylon, or other materials such as oils, waxes, rubber and plastics. In these cases the dyes may form a chemical union with the substance being dyed or it may become associated with it in an intimate physical union. Dyes, which are more or less soluble in water or may be made so simply, by a simple chemical reaction such as reduction, generally are used for dyeing and printing of fibres

and related materials. Dyes of solvents, oils, waxes or plastics are either soluble in these media or else so finely divided that they may be effectively dispersed throughout to give high colour strength. These insoluble colouring substances are called pigments¹⁰¹.

1.2.2 CLASSIFICATION OF DYES:

It has been found convenient to classify organic dyestuffs in the following two fundamentally different ways:

1. Based on method of application of the dyes.
2. Based on the chemical constitution of the dyes.

The first categorizing is very useful to the dyers who are mainly concerned with the process of dyeing. Moreover, this classification gives the diverse methods of dyeing different fibres with various dyes. Thus, the dyes are classified into the following categories:

- (i) Acid dyes, (ii) Basic dyes, (iii) Direct dyes, (iv) Mordant dyes, (v) Ingrain dyes, (vi) Vat dyes (vii) Sulphur dyes, (viii) Synthetic fibre dyes and (ix) Other synthetic dyes.

The second classification is mainly useful for those chemists who are mainly interested in chemical constitution of the dyes. O. N. Witt¹⁰² was the first who suggested a classification of the dyes according to chromophore or the essential colour-producing group present in the dyes. But a number of dyes contain the same chromophoric group and so it became necessary to adopt a classification on the basis of the characteristic structural groups present in the dye molecule. This chemical classification therefore divided all the dyes into the following principal groups described below under two main classes: Homocyclic hetero ring absent and Heterocyclic - at least one hetero ring present.

(A) HOMOCYCLIC DYES:

- (a) Anthraquinone dyes, (b) Azo dyes, (c) Azomethine dyes or benzylidene dyes,
- (d) diphenylmethane dyes (e) Ethylenic dyes, (f) Ketoimine dyes, (g) Nitro dyes,
- (h) Nitroso dyes, (i) Pyrazolone dyes, (j) Quinonimine dyes and (k) Triphenylmethane dyes

(B) HETEROCYCLIC DYES

(l) Acridenes, (m) Azines, (n) Azoxy and nitrosostilbene dyes, (o) Flavones, (p) Indigoids, (q) Oxazine dyes, (r) Quinoline dyes:

- (i) Cyanines, (ii) Isocyanines, (iii) Pynacyanols, (iv) Dicynines, (v) Carbocyanines;
- (s) Sulphur dyes:
 - (i) Thiazine dyes, (ii) Thiazoles, (iii) Sulphur blacks;
- (t) Phthalocyanines, (u) Xanthen dyes:
 - (i) Fluorones, (ii) Phthaleins, (iii) Pyronines, (iv) Succineins, (v) Rosamines and (vi) Rhodamines.

1.3 NOMENCLATURE SYSTEM:

Unfortunately, there is no uniformity in the nomenclature of the synthetic dyes. In most cases they bear the name given to them by their manufacturers. Furthermore, each dyestuff may have a number of names or different dyes may be known by the same names. In the Colour Index of the Society of Dyers and Colourists¹⁰³, however each dye is given an individual number called the colour Index Number abridged as C.I.No.

1.3.2 PHTHALEINS:

Baeyer¹⁰⁴ first discovered these dyes in 1872 as a new class of dyes. He prepared GALIEN, FLUORESCEIN and PHENOLPHTHALEIN by condensing phthalic anhydride with pyrogallol; resorcinol and phenol respectively in presence of a dehydrating agent like sulphuric acid or zinc chloride. Baeyer established that

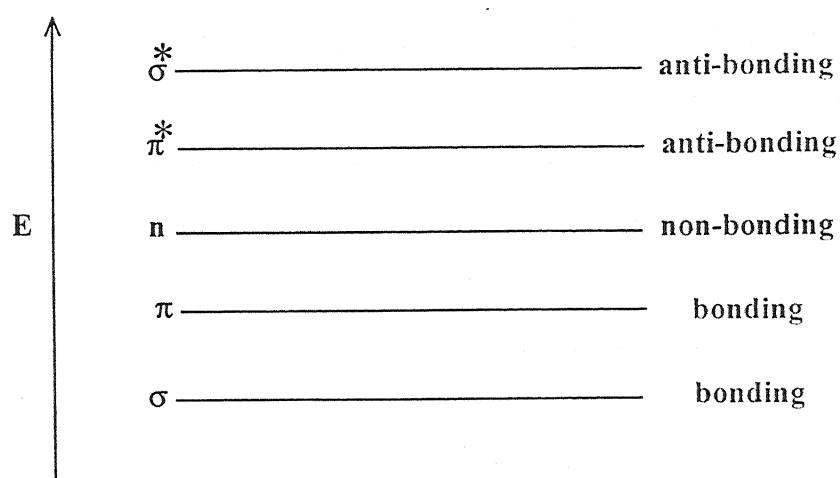
the parent member of the group phenolphthalein was a dihydroxy derivative of phthalophenone which in turn could be degraded to triphenylmethane. Thus, he illustrated that phenolphthalein was a derivative of triphenylmethane and followed analogous arguments¹⁰⁵ for fluorescein and for similar dyes called rhodamines. Baeyer classed them under triphenylmethane dyes which some authors¹⁰⁶ still follow. Elsewhere,¹⁰⁷ only phenolphthalein, its tetraiodo derivative and sulphophthaleins constitute the group, phthaleins and fluorescein its derivative uranine, eosine, mercurochrome, and rhodamines constitute another group called xanthenes. Both phthaleins and xanthenes, in turn, form a subclass of triphenylmethane dyes.

According to Baeyer's all the dyes prepared by the condensation of phthalic anhydride with different phenols, aromatic hydroxy compounds are grouped as phthaleins. Pyronines, rhodamines, and other similar dyes, which could be prepared in a similar manner that used for the preparation of phthaleins, included, contain a characteristic dibenzo- 1,4 – pyran nucleus. Dibenzo- 1,4 – pyran is called xanthen,¹⁰⁸ which is an anhydride of o – o' dihydroxydiphenylmethane. From xanthen these dyes can be derived by introducing auxochromes¹⁰⁹ into positions 3 and 6, i.e. in para position with respect to carbon atom linking the two benzene rings. Therefore, in the classification used herein these dyes are grouped as xanthen dyes or xanthenes¹¹⁰.

In fact, phenolphthalein, although a thalein, is not a xanthen derivative¹¹¹. Yet, generally, xanthenes are prepared¹¹² like phenolphthaleins by the method mentioned earlier.

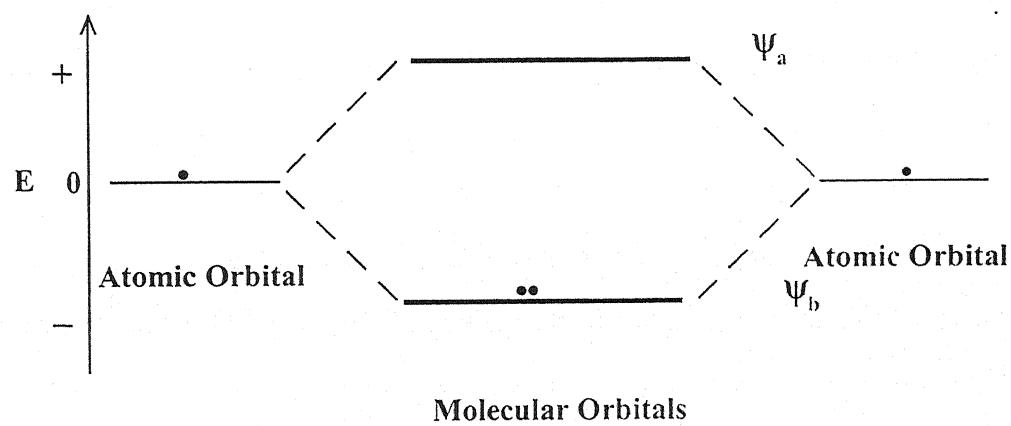
1.4 COLOUR AND CONSTITUTION OF ORGANIC MOLECULES:

It is commonly believed that colour is generated by the absorption of certain wavelengths of the visible light. Organic compounds with extensive conjugation absorb certain wavelengths of light because of $\pi - \pi^*$ and $n - \pi^*$ transitions. We do not observe the colour absorbed but we see its complement that is reflected. A complementary colour sometimes called a subtraction colour is thus the result of



Electronic Energy levels in Ground and Excited states

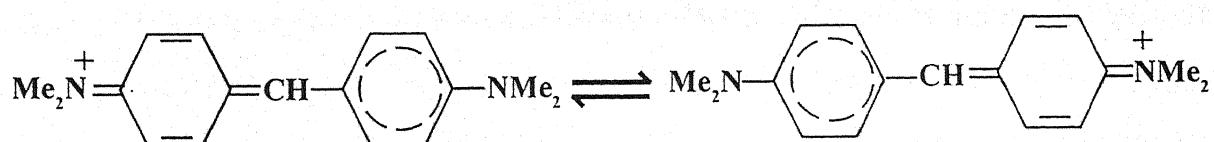
FIGURE 1.06



Molecular Orbitals

COMBINED ENERGY LEVEL DIAGRAM

FIGURE 1.07



CLASSICAL STRUCTURES OF MICHELERS HYDRO BLUE

FIGURE 1.08

the subtraction of some of the visible wavelengths from the entire visual spectrum. Before the theories of electronic transition were developed, it was observed that some types of organic structures give rise to colour while others do not. The structures that are necessary for colour, the unsaturated groups¹¹⁵ can undergo $\pi - \pi^*$ transitions, were called chromophores by Witt¹¹⁴ in 1876 (Greek Chroma – colour and phoros - bearing). These he specified as nitro-, nitroso-, azo- and carbonyl- groups that he suggested fall in this category. Molecules containing such groups e.g. nitrobenzene and azobenzene were referred to as chromogens since they had the potentiality of colours even if they were not in themselves intensely coloured. Witt observed that the presence of some other groups caused an intensification of colours. These groups were called the auxochromes (Greek auxanein – to increase). These groups which were typically polar such as hydroxyl- or amino – did not in themselves produce colours, as we know now that they can not undergo $\pi - \pi^*$ transitions, but could produce hypsochromic effect i.e. a shift in the absorption bands to shorter wave lengths, or a bathochromic effect where the shift is in the opposite direction, i.e. to longer wave lengths, as they can undergo transition of n electrons. However, in practice, intense colour can be obtained without the presence of auxochromic groups and it has since been shown that this concept has nothing of scientific significance. The theories of Graebe, Leibermann, Witt, Neitzki¹¹⁵ Armstrong¹¹⁶ etc. were the results of successful attempts to determine the molecular structure of organic compounds and interpretation of colours in terms of chemical structure without much regard to its physical causation.

During the early years chemists were intrigued by the elusive relationship between the absorption spectra and the molecular structure and therefore the progress was severely hampered for want of suitable theory for the light absorption process itself. Today, thanks to the advent of quantum theory, we are in a more fortunate position, and mathematical treatments of varying levels of sophistication are available for the prediction of absorption spectra. Equally important are the

qualitative treatments of light absorption, which have stemmed from the valence bond and the molecular orbital theories and which can be used to predict qualitatively the effects of structural changes on the absorption spectra of a molecule.

B.1 THE MECHANISM OF ABSORPTION OF LIGHT BY MOLECULES:

It is worthwhile to point out here that a complete and satisfactory explanation of the colour of the organic compounds was found to be associated with absorption and transmission of light in general with the spectra of the molecule. The absorption of light was recognized to be associated with certain process of molecular energy changes and the process could also take place with many other substances besides those as appeared coloured to the human eyes. The colour as it appears to the human eyes is only a special case of the general feature of general phenomenon of absorption of electromagnetic waves. The colour of the substance for which the human eye is sensitive is determined by the selective absorption of light consisting of those waves. The phenomenon of light absorption is not limited to the visible part of the spectrum only but takes place in the ultra violet and infra red regions as well. Since white light imparts different colours to different chemical compounds, it is obvious that colour is a function of the chemical constitution of the molecules.

The wave particle duality of matter when applied to the electromagnetic radiation and to atomic particle forms the basis of quantum theory that uses the famous de Broglie relation

$$P = h/\lambda \dots \text{Eq. 1}$$

where p is the momentum of the particle, λ is its associated wavelength and h is the Planck's constant.

The absorption and emission of light by matter¹¹⁷ is explained by the wave properties of light. An electromagnetic wave is characterized by an electric vector E and a magnetic vector H which form a mutually perpendicular set of axes with the propagation of the vector C . The absorption of light arises mainly through an

interaction of electric vector of light with the electrons and nuclei in the molecule. The magnetic vector is only important for an understanding of phenomenon of optical rotation. A molecule initially in a state of E_a can absorb light of frequency ν , provided there is existing a state E_b that has greater energy than E_a by an amount E which satisfies the relation

$$E = E_b - E_a = h \nu = hc/\lambda \quad \dots \quad \text{Eq. 2}$$

and it is said that the molecule has absorbed a photon of energy $h\nu$ and is in the excited state E_b . The stability in the excited state is limited and after a very short time e.g. less than 10^{-8} second. The excited molecule dissipates its excitation energy and comes back to the ground state E_a .

A molecule can exist in many excited states corresponding to the changes in its rotational, vibrational and electronic energy levels. And all these energies are quantified. Therefore the absorption spectra can be further classified¹¹⁸ into three types:

1. Pure rotational spectrum which is associated with the changes in the rotational states of the molecule without the simultaneous changes in the vibrational and the electronic states. Since the separation between the various rotational levels are relatively small, it follows from Equation 2 that the corresponding frequencies are so relatively low that pure rotational spectra of all substances occur in the far infra red and the microwave regions.
2. Rotational vibrational spectrum is associated with transitions in which the rotational and the vibrational states of the molecule are altered, but the electronic state remains unchanged. The energy differences are relatively greater than in pure rotational spectrum and, accordingly, the absorption occurs at shorter wavelengths i.e. in the near infra red region.
3. Electronic spectrum that arises from the transitions between the electronic states changes both the vibrational and the rotational levels. Therefore, a broad-spectrum band instead of a sharp line is observed. Relatively large differences are involved in the electronic spectra, which occur at still shorter wavelengths,

i.e. in the ultra violet and the infra red region.

Since the electrons can only be raised up to certain energy levels, ΔE must have some definite value; i.e. absorption of light by a molecule is not indiscriminate and discontinuous, but selective and gives rise to colour. Apart from the frequency of the absorption band, colour also depends upon the intensity of the absorption that in turn depends upon probability of transition between the two energy levels concerned. The probability of the photon being absorbed depends upon the magnitude of the transition dipole moment between the two concerned energy states.

The light absorption by a molecule¹¹⁹ can only occur when dipole moment changes in a molecule. The more symmetrical the molecule, smaller is the probability of the transition dipole and, therefore, the less likelihood of absorption of light by the molecule. Calculations have shown that greater is the transition dipole, greater is the intensity of absorption. The introduction of a group in a molecule that decreases the symmetry will thus increase the transition dipole and consequently increase the intensity of absorption. At same time, however, new 'resonance paths' may be introduced, and hence, not only a change in the intensity of absorption occurs, but also there is shift of the band to longer wave lengths.

1.4.1 THEORETICAL MODELS FOR CALCULATING LIGHT

ABSORPTION:

Absorption of ultra violet and visible light by a molecule causes an electronic transition from a lower to a higher energy level; or more exactly causes an excitation from the highest energy level in the ground state to the lowest permitted energy level in the excited state as shown in figure 1.06. Compounds where the valence electrons are involved in sigma bond formation, such as saturated hydrocarbons, only show absorption due to excitation of an electron to a σ^* antibonding or a higher orbital. The energy requirements are high, above 150 kcal

mole⁻¹ and absorption occurs below 2000 Å to 200 nm. This type of excitation process is referred to as $\sigma \rightarrow \sigma^*$ transition, where the asterisk denotes an excited state. In compounds containing lone pair electrons; O, N, S which are not utilized in bonding, the energy requirements for excitations are less since these electrons are generally less strongly held. The $n \rightarrow \pi^*$ transitions (following the nomenclature of Kash¹²⁰) in simple molecules thus gives rise to spectral bands at the longer wavelengths than those associated with $\sigma \rightarrow \sigma^*$ to $\pi \rightarrow \pi^*$ transitions. Proton addition to the non-bonding electron pair in O, N, or S atoms causes the disappearance of the band at long wavelengths confirming that these non-bonding electrons take part in the excitation process. $\pi \rightarrow \pi^*$ transitions occur in the molecules containing double bonds in which there is an overlap of p – orbital causing formation of π – bonds. Because the overlap of p – orbital is not as great as in σ – bonding, the $\pi \rightarrow \pi^*$ transitions generally occur at the wavelengths intermediate between those of $\sigma \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions, i.e. in the near ultra violet and the visible region of the spectrum.

Thus, from the foregoing discussion, it becomes clear that to understand the colour of a compound, it is necessary to have a knowledge of the electronic structure of the molecule and its effect on the absorption of light in the visible and the near ultra violet region of the spectrum. For this purpose, three main theoretical approaches to the problem have been made.

1.4.2 MOLECULAR ORBITAL THEORY (MO) THEORY:

It is first necessary to explain the term 'antibonding', which arises from the concept of the molecular theory. It is best illustrated in the case hydrogen molecule. When the two constituent atom A and B are at equilibrium distance characteristic of the stable molecule, the two atomic orbitals ϕ_A and ϕ_B , each of which accommodates one electron, will combine to form two molecular orbitals. The first of the lowest energy, is represented by the wave function ψ_B , and is called the bonding orbital.

This orbital has characteristics separately possessed by ϕ_A and ϕ_B , and may be written in a simplified treatment as a linear combination of the two,

$$\Psi_B = \phi_A + \phi_B$$

The molecular orbitals arise from the atomic orbitals without the consideration of the electrons they have to accommodate. This treatment is referred to as Linear Combination of Atomic Orbitals. The second molecular orbital Ψ_A is formed in hydrogen with the condition that

$$\Psi_A = \phi_A - \phi_B$$

This Ψ_A is the antibonding molecular orbital. The electron density or probability of finding an electron at a given point in this system is given by Ψ^2 . The charge distribution in both molecular orbitals is cylindrically symmetrical. In the bonding orbital, the electron density is greatest between the two nuclei. In the antibonding orbital it is low between the two nuclei and the more stable configuration of the molecule is when the two nuclei are farther apart. It is this difference between the two molecular orbitals, which determines wavelength of the absorbed or the emitted light.

The energies of Ψ_A and Ψ_B molecular orbitals may be represented by the combined energy level diagram (figure 1.07) where the electrons, x , contributing to separate functions ϕ_A and ϕ_B are shown combined in the bonding molecular orbital Ψ_B . It is assumed that the overlap of Ψ_A and Ψ_B in this case is zero. The two molecular orbitals Ψ_A and Ψ_B lie at equal difference in energy above and below the individual atomic orbitals. When the degree of interaction or overlap is positive, it can be shown that the antibonding orbital is displaced to higher energy above initial energy and the bonding orbital is displaced to a lower energy to the same extent. Dewar¹²¹ has extended this method of energy demonstration to hybrids of classical structures, i. e. where the wave functions ϕ_A and ϕ_B differ in energy, using as an example two classical structures of Michler's Hydro Blue (figure 1.08). The interaction of the two classical structures will give rise to two hybrid states, one of higher energy and the other of lower energy. The energy difference will be

smaller when the energies of classical structures are comparable i. e. mesomeric; and the absorption occurs at longer wavelengths than when the classical structures have greater divergence in energy.

In the ground state of hydrogen, according to Pauli's Exclusion Principle, the electrons have opposing spins and the state is known as singlet state. Both electrons occupy the Ψ_B bonding molecular orbital. In the first excited state, one electron is transported to an antibonding orbital. Since the electrons are now in different orbitals, the exclusion principle is no longer applicable and the electrons may now either be paired to give an excited singlet state, or unpaired to give a triplet state. In the latter case, there are three possible states all having the same energy since the z - components of the spin quantum numbers of the two electrons may be both +1/2 or both -1/2 or one may be +1/2 while the other is -1/2. The z - component of the resultant angular momentum may thus be 1, 0, or -1 and the three possible states are known jointly as the triplet state. A further excited state is possible when both the electrons occupy the antibonding orbital. Since the exclusion principle is now applicable, this must be, of necessity, a singlet state, the excited singlet state.

This elementary MO treatment can be extended to molecules which are electronically more complex, such as nitrogen oxide and carbon monoxide, but which, as molecules, are relatively simple, provided due account is taken of hybridization in the molecular orbital formation. For more complex molecules, however, further simplifications and assumptions have to be made. In applying the theory it is necessary to neglect all overlap integrals between non-adjacent atoms to average electron repulsions and to assume they are unchanged by the excitation process.

Further according to the theory of molecular orbitals¹²³⁻¹²⁴ the absorption of the u.v. and the visible light corresponds to the electron cloud of a molecule, resulting in the formation of electronically excited state. According to quantum theory, a molecule can exist only in a limited number of discrete energy states. The electronic

structure of a molecule can be built up by the feeding of electrons one after another in the lowest available quantum states in accordance with the Aufbau Principle. A concept of united atom i. e. an atom whose atomic number is equal to the sum of the two separated atoms is helpful to understand the filling of electrons in the MO. The electrons, which in the united atom occupy in the excited state, are the antibonding electrons and those that do not are bonding electrons. The electrons in the atoms that remain unaffected by the process of molecule formation are said to be nonbonding electrons.

It is possible to consider the phenomenon of light absorption from the point of view of the molecular orbital theory. A molecule is excited when one electron is transferred from an orbital of lower energy to one of higher energy. Such transitions can occur only between permitted orbitals. In a molecule a g state must go to a u state, or vice versa; transitions $u \rightarrow u^*$ and $g \rightarrow g^*$ are forbidden. Here u and g bear their usual meaning.

The ethylene molecule in its ground state has, in addition to a σ bond, a π bond i.e. a π_g orbital (bonding molecular orbital) in which there is the first excited state, π_u orbital (antibonding molecular orbital). If one electron is excited from π_g to π_u a large amount of energy is required and the molecule therefore absorbs in the u.v region

In compounds containing more than one double bond and that too in conjugation, delocalization of bonds takes place and the molecular orbital formed covers all the carbon atoms of the conjugated system. The electron, therefore, has greater freedom of movement than in localized bonds and the total energy of the system is lowered which decreases the energy difference, Δ between the highest occupied and the unoccupied orbitals. Thus, as the conjugation extends, the absorption of light takes place at yet longer wavelengths.

Benzene molecule is symmetrical with all the carbon atoms having equal charges of unity and hence there is no transition dipole in the benzene molecule. It is not expected to absorb the light and hence it is colourless. However, a weak absorption

in the u.v region is expected and so exhibited. Nitrobenzene is not symmetrical and has unequally charged carbon atoms. Unequal charge produces a definite dipole moment in the molecule of nitrobenzene. The result is high transition dipole and absorption at longer wavelengths.

Furthermore, since nitrobenzene has an extended conjugation, the energy difference between the highest occupied orbitals is decreased, and therefore, it absorbs at longer wavelengths than benzene.

Nitroaniline (orange red) having more extended conjugation and greater separation of charge absorbs light at still longer wavelengths than nitrobenzene and aniline. Thus, in general, any such group, which exists in conjugation with benzene ring, happens to practically cause the shifts in the frequencies of the absorbed light towards the lower region or the wavelengths towards the longer regions. This effect of shifting of absorbed light towards the lower regions of the spectrum or those in wavelengths of the absorbed light towards the longer region in the electromagnetic spectrum, is what we understand and name as the Red Shift or the Bathochromic shift, or the Bathochromic Effect. These shifts, if effected in the directions exactly opposite to those mentioned before, are said to be the Blue Shift, or the Hypsochromic Shift or the Hypsochromic effect.

Despite the fact that the molecular orbital method appears to be more promising from a quantitative point of view, and it has been possible to calculate the light absorption of many molecules by the ingenious applications of the great Molecular Orbital Method resulting in good agreement that has been obtained between the calculated and the observed values¹²⁵, the Valence Bond Method as applied to absorption of light and prediction of colour proves quite satisfactory for qualitative purposes; and, therefore, one can not do well in keeping away from it. Thus, the valence bond approach is being discussed in the following section.

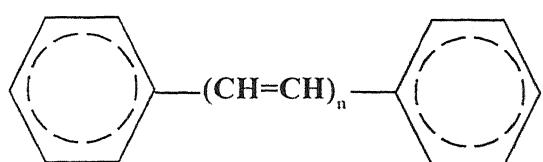


FIGURE 1.09

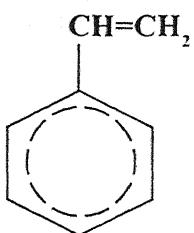


FIGURE 1.10

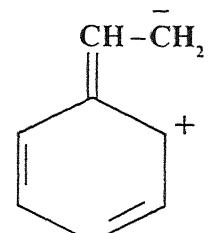


FIGURE 1.11

Table 1.01

n	0	1	2	3	4	5	6	7
$\lambda_{\text{max.}}$	2515	3190	3520	3770	4040	4240	4450	4650

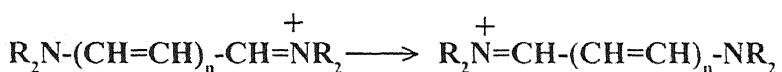
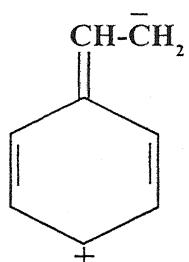


FIGURE 1.13a

FIGURE 1.13b

FIGURE 1.12

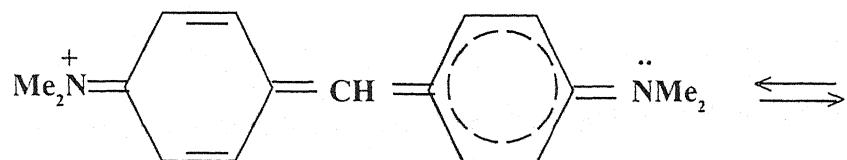


FIGURE 1.14a

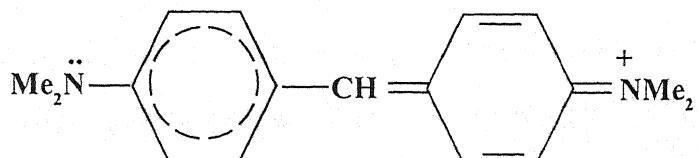
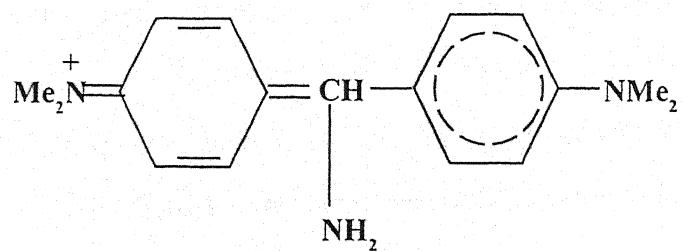


FIGURE 1.14b



Auramine

FIGURE 1.15

1.4.3 VALENCE BOND (VB) THEORY:

The second theoretical model proposed for correlation of molecular structure and its spectra is the Valence Bond (Resonance) Theory.

This theory is concerned with the contribution made to spectra by the ionic states, must of necessity include approximations since the number of ionic structures considered in any complex organic molecule has to be limited. For example, there are over a hundred possible ionic structures of benzene involving only two p electrons, in addition to the Kekule and the Dewar structures. In order to compare the molecular orbital and the valence bond treatments of benzene, all these structures should be taken into account. With still more complex molecules, the number of ionic configurations greatly increases.

Although the valence bond theory can predict the location of the absorption bands and molecular orbital theory the intensity of the absorption of the simple molecules, it has still to be shown that the bands for which the calculations have been made are in fact correctly assigned¹²⁶

The early studies of light absorption have observed that certain molecules absorbing in the visible region could be represented by two equivalent resonating structures, between which an oscillation of bonds was believed to occur. Burry¹²⁷ was the first to suggest that the colour was actually due to such oscillations. However, due to rapid development of quantum theory, this observation was modified by a number of investigators. Lewis and Calvin¹²⁸, Pauling^{129, 130}, Forster¹³¹, and Knott¹³² have proposed that the colour of the compound is associated with resonance between two or more structures which differ by the displacement of an electron charge from one atom to the other of the molecule of the compound. Lewis and Calvin have been able to show that colour also depends upon the number of electrons involved in oscillations. Larger the number of such electrons, the deeper will be the colour.

It has been found that increased conjugation in a molecule shifts the absorption

band towards longer wave lengths and thus it deepens the colour, for example table 1 shows this shift as the value of n in figure 1.09 changes. Obviously, the factors responsible for decrease in ΔE will shift the absorption band to longer wavelengths. Resonance among charged structures lowers the energies of both the ground and the excited states and since charged structures contribute more to the excited state than the ground state, the lowering of the energy will be more prominent in the former than the latter. Thus, a greater resonance among the various charged forms results in the deepening of colour.

It can be safely inferred from the foregoing discussion that a given chromophore will not necessarily give absorption bands in the same position of the spectrum; the rest of the molecule also affects it. Benzene has a definite u. v. absorption, 255 nm, ethylene has 185 nm and allylbenzene 249 nm, which is equivalent to the superimposition of spectra of benzene and ethylene. However, styrene has a quite different spectrum, 282 nm where the fine structure of benzene is absent.

Therefore, it can be observed that in styrene, the benzene nucleus is not in the same state, as it was in allylbenzene itself. This observation can be explained by assuming styrene to be a resonance hybrid of the structures in figures 1.10, 1.11 and 1.12.

The cyanine dyes, studied by Brooker and coworkers¹³³ are intensely coloured substances exhibiting a high degree of resonance. These dyes can be represented by the general structures 1.13a and 1.13b.

If aromatic ring systems are made part of conjugated chain of a cyanine, the characteristic properties of the chromophore are not altered. Thus, they will still be isoconjugate with an alternate odd hydrocarbon anion, and will absorb at long wavelengths by virtue of the presence of a nonbonding molecular orbital. The di- and tri-aryl methane dyes are examples of this type.

Michler's Hydrol Blue, a diaryl methane dye, which is a resonance hybrid of two equivalent structures 1.14a and 1.14b, absorbs at 607.5 nm in 98% acetic acid.

The auramine 1.15, an important commercial dye of diaryl methane series, which

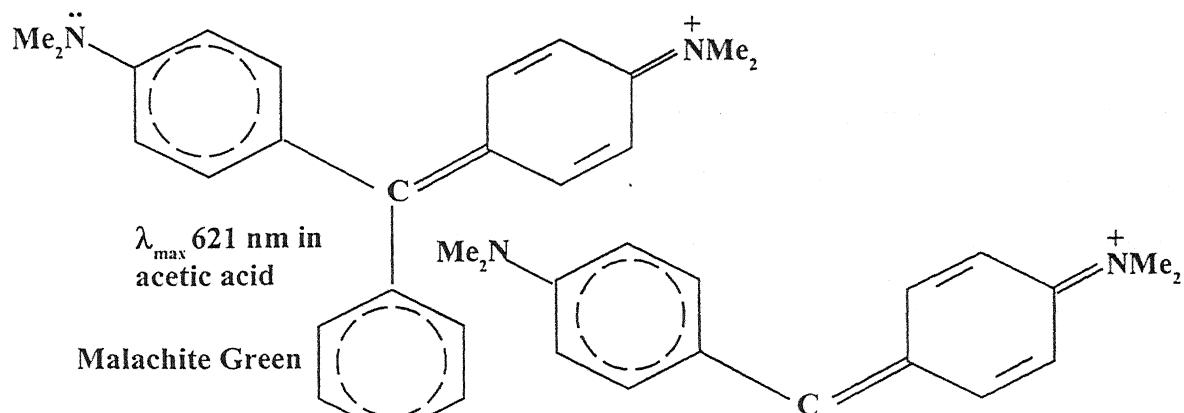


FIGURE 1.16



FIGURE 1.17

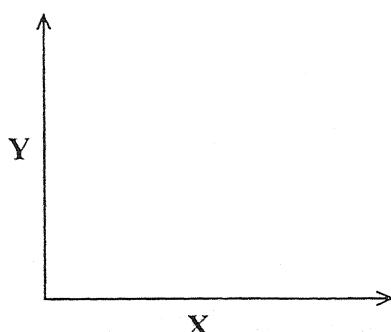


FIGURE 1.18

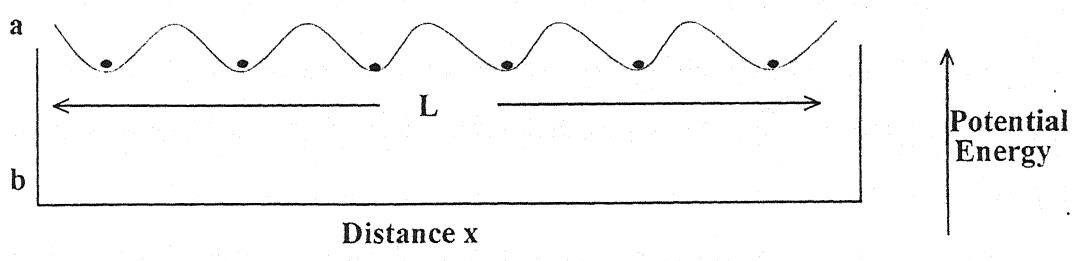


FIGURE 1.19

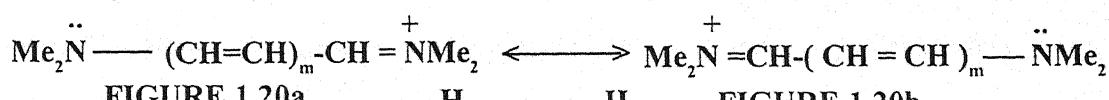


FIGURE 1.20a

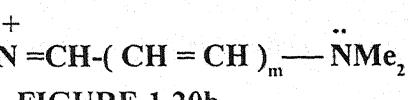


FIGURE 1.20b

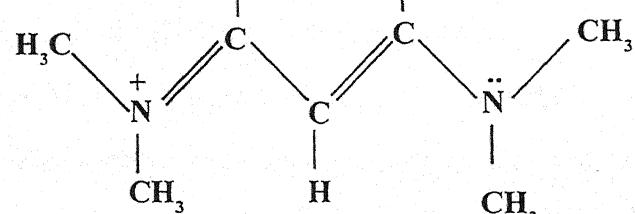


FIGURE 1.21a Cyanine molecule

is formed by the attachment of an amino group to the central carbon atom of Michler's Hydrol Blue, shows large hypsochromic shift that results from the strongly electron donating amino group and absorbs at 434 nm in ethanol. Substituents other than amino group exert a hypsochromic shift related to electron donating capacity e. g. the attachment of a weaker ethoxy group to the central atom of Michler's Hydrol Blue gives a smaller shift, and the dye is purple, $\lambda_{\text{max.}} 525$ nm.

The triaryl methane dyes, on the other hand, can be divided into two distinct types; those with two terminal amino groups, e. g. Malachite Green, Figure 1.16, and those with three terminal amino groups, e. g. Crystal Violet, Figure 1.17. From the foregoing discussion it is expected that increased number of resonance forms would deepen the colour. But the case of Malachite Green and Crystal Violet proves contrary to the expectations as the colour of the former is deeper than the latter. Malachite Green has two resonating forms where as crystal violet has three. The former shows two absorption bands; one at longer wavelength $\lambda_{\text{max.}} 621$ nm in 98% acetic acid, as expected for the attachment of the neutral conjugating group at any position in the chromophore; and a second band at a shorter wavelength, $\lambda_{\text{max.}} 427$ nm, as this provides a yellow component to the colour, the dye is green rather than blue. Polarization studies have shown that the two transitions are polarized along mutually perpendicular axes¹³⁴. The longer wavelength band is due to polarization along X-axis and the shorter along Y-axis.

Let us now reflect on hypsochromatic shift shown by Crystal Violet when a dimethyl amino group is substituted in Malachite green. As per resonance theory Crystal violet ion has a high symmetry and consequently a number of levels will have the same energy although the total number of levels has actually increased and are responsible for the remarkable hypsochromic effect. The average separation of the oscillating charges is, however, increased. Thus, the band is displaced to the shorter region, while intensity has increased due to increased transition probability proportionate to increased number of corresponding levels. Lewis and Calvin

proposed that the oscillation of a charge along one direction only is responsible for colour. In Malachite Green all positive charge is involved in linear oscillations while the Crystal Violet positive charge can oscillate linearly, horizontally as well as perpendicularly, vertically. Thus, 2/3 positive charge is effectively oscillating horizontally in Crystal Violet. Hence, Malachite Green has a deeper colour than Crystal Violet.

1.4.4 FREE ELECTRON MOLECULAR ORBITAL (FEMO) THEORY:

The application of MO and VB theories to dyes of practical importance and interest which have complicated structures and their colour is strongly affected by even a slight structural change, requires ruthless simplification to obtain even the most general agreement with the observed facts. A third theoretical treatment which on the one hand is highly simplified, and still based on highly valued quantum mechanical treatment on the other, and also avoids rigorous mathematical dilemma; which has been applied to such complex chromophores with a great degree of success is the one known as Free Electron Gas Method, Free Electron methods¹³⁵⁻¹³⁶, or FEM or Free Electron Molecular Orbital , FEMO method¹³⁷. This was first proposed by Sommerfield¹³⁸ to describe the metallic state and later extended to organic molecules by Bayliss¹³⁹, Simpson¹⁴⁰, and notably developed by Kuhn¹⁴¹⁻¹⁴² and Platt¹⁴³. In its application, this model is limited to consideration of conjugation of π -electron systems; but then dyes are considered to owe their colour to these electrons, this theory will be treated in greater detail.

Simple of all the molecular methods for conjugated organic molecules, as this theory is, remarkably successful too in calculating transition energies in certain cases. Quite like the valence bond and the molecular orbital treatments, in this model too, all the carbon atoms and all the hydrogen atoms are supposed to lie in one plane so that all atomic orbitals are of either σ or π type. The fundamental assumption, rather approximation, in this treatment is the sigma-pi-separation

principle¹⁴⁴, i.e. the sigma and pi electrons can be treated separately and independently. Consequent upon this specifically characteristic assumed feature of this treatment, and that the pi electrons are comparatively free to move within the conjugated system and, provided that this movement is only in the direction of the conjugated chain, their behaviour can be represented by that of an electron in a box or a potential well. Figure 1.19 represents the potential energy of such an electron, where the minus occurs at the positions of the individual carbon atoms along the chain. The energy shown in the lower part of the said figure represents an assumed constant potential along the chain length. The terminal potential barriers are situated at an arbitrary distance beyond the extreme carbon atoms. The quantum mechanical solution of a wave equation for a particle moving under these conditions is,

$$\psi_n = 2/L \cdot \sin [\pi n / L] \cdot x$$

where $0 < x < L$, L is the wavelength, x is the distance along the well and n is a quantum number (1, 2, 3, 4,.....etc.). For each value of ψ_n there is a corresponding energy,

$$E_n = n^2 h^2 / 8mL^2 \quad \text{Equation .1}$$

Where h is Planck's constant and the m is the mass of an electron. In a system consisting of alternate double and single bonded carbon atoms, each carbon atom contributes one pi electron. If the total number of pi electrons is N , then in the ground state are the $N / 2$ levels of the lowest energy since each level is doubly occupied by the electrons having opposing spins = $1/2$, $-1/2$, according to Pauli's exclusion principle. As no limitation is placed on the number of the possible levels, all others except filled $N / 2$ levels will be empty. When the molecule or the ion absorbs light, this corresponds to one electron jump from the highest filled level with quantum number $n_1 = N / 2$ to the next higher energy level, i. e. the lowest empty level with quantum number $n_2 = N / 2 + 1$. The energy change or the excitation energy for this transition is therefore,

$$E = E_{N/2+1} - E_{N/2} = (N+1)h^2 / 8mL^2 \quad \text{E.2}$$

Since $\Delta E = h\nu = hc / \lambda$, where c is the velocity of light λ is the wavelength in centimeters,

$$\lambda = 8mcL^2 / h(N + 1) \quad E.3$$

This equation can therefore be applied to any linear conjugated system provided that the number of the double bonds is known and assignment of L is made. Since λ is proportional to L^2 , correct values for L are important. If need be the above treatment may be extended to three dimensions by supposing the electron to be residing in a three dimensional box.

1.4.5 APPLICATION OF THE FREE ELECTRON MODEL TO BUTADIENE:

The pi electron structure of 1,3- butadiene is obtained by assigning two electrons of opposing spins to the lowest orbital and two similarly spin paired electrons to the second lowest. The absorption of light is then assumed to involve the promotion of one of these four electrons to any of the higher orbitals. Equation 3 can then be used to calculate transition energies. The only uncertain parameter is L , the length of the conjugated chain, say that of the potential well. It is usual to regard L as equal to the length of the conjugated chain molecule assuming that the molecule is distorted into a straight line plus one additional bond length at each end of the molecule. For example, 1,3 - butadiene has an average bond length of 1.4 Å, which gives a value of 7 Å for L . Using aforesaid equation for 1,3 - butadiene a first transition energy of about $3.0 \times 10^4 \text{ cm}^{-1}$, or a wavelength of 325 nm is found. The experimental value, 220nm, may seem indicative of poor agreement, but in view of the many gross approximations inherent in the FEM treatment, and its greater simplicity of approach, the agreement is supposed to be remarkably good.

1.4.6 USAGE OF FREE ELECTRON MODEL ON CYANINES,

AZACYANINES, AND BASIC DYES:

The series of compounds known as cyanines typified by Figure 1.20 are ideally

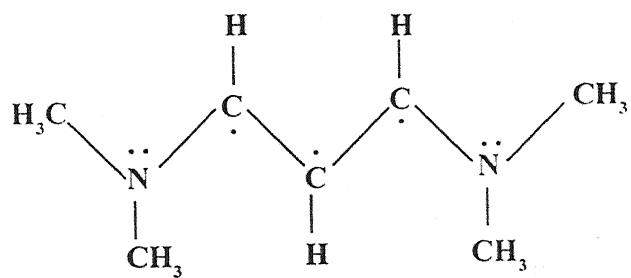


FIGURE 1.21b Cyanine sigma skeleton in common plane

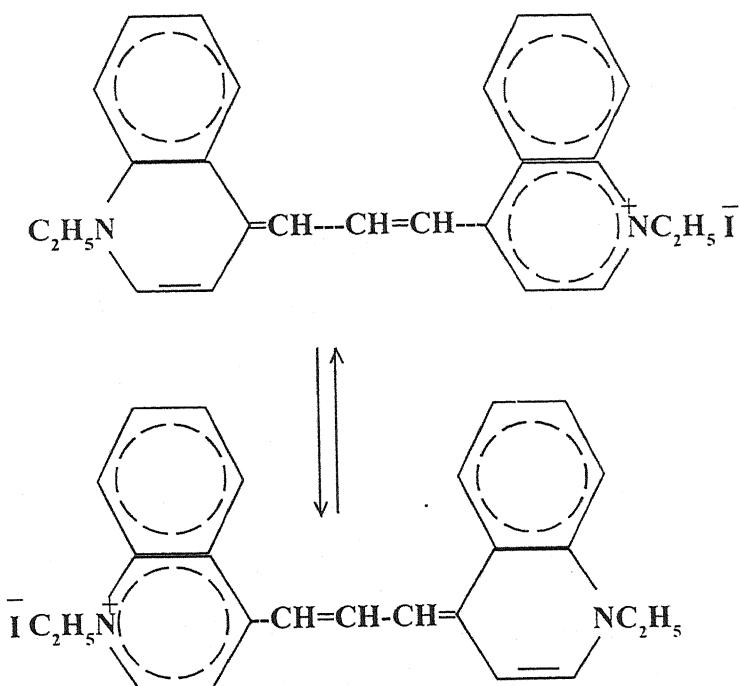


FIGURE 1.22

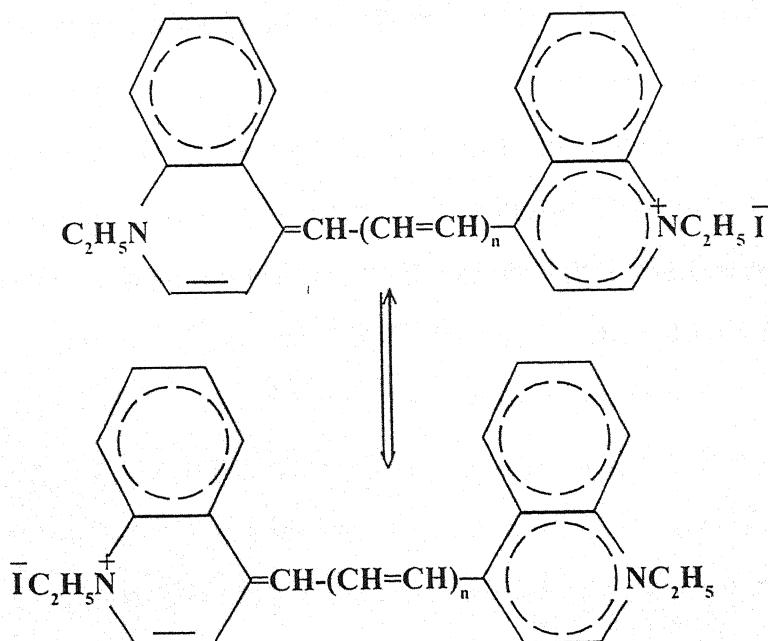


FIGURE 1.23

suited for this method, since they show appreciable bond uniformity that arises from resonance.

A symmetrical cyanine dye molecule such as Figure 1.21a and 1.21b may be considered here in order to find a plausible explanation for its electronic absorption band in the visible region, here the C, N, and hydrogen atoms are linked by sigma bonds and are located in a common plane.

Each carbon and each nitrogen atom uses its three valence electrons to form the sigma bonds, pi electronic system in the molecule is formed by the contribution of the fourth valence shell electron of the each carbon atom and the remaining electrons of the two terminal atoms of nitrogen. These electrons are placed in the electrostatic field of the molecular skeleton. They will be attracted to the positive charges of C and N atoms, but their wave function must not have a node at all points of the plane of the molecule. They form an electron gas, which in the shape of a charge cloud stretches along the cyanine chain, both above and below the plane of the molecule. N has five electrons in the said cyanine three are used to form sigma bonds, thus N atom with no charge sign contributes two electrons to the pi electron gas and that with a formal positive charge yields one pi electron. In addition to this, each carbon atom contributes one pi electron, and we find a total of six pi electrons or three pi electron pairs in this case. Now a single pi electron is considered in the electrostatic field of the rest of the molecule and it should be assumed for a moment that it could only move in the direction of the zigzag line connecting C and N atoms in the chain. The potential energy of the electron is then roughly constant along the chain since the electron is practically in the coulomb field of the nearest C or N atom only, while the field of more distant C and N is neutralized by other pi electrons. And, consequently, this electron can move almost freely along the zigzag line, but not beyond the ends of the chain except when the chain itself stretches. Thus, this electron is in the same condition as a free electron considered earlier in a one-dimensional box and the length L of the chain corresponds to the length of the box. It must be noted, however, that

the component of the motion of the pi electron in the direction perpendicular to the zigzag line connecting C and N atoms in the chain, has been neglected here(Figure 1.19).

In the normal state of the molecule, the three electron pairs present in the resonating chain occupy the three lowest levels. The light absorption is caused by transition of an electron from the highest occupied molecular orbital (HOMO) with $n = 3$ to the lowest unoccupied molecular orbital (LUMO) with $n = 4$.

Accordingly, the energy difference ΔE between these states is,

$$\Delta E = E_4 - E_3 = (4h)^2 / 8mL^2 - (3n)^2/8mL^2 = 7h^2/8mL^2 = 6.1 \times 10^{-12} \text{ ergs}$$

$$\text{and, } \lambda_{\max} = h c/\Delta E = (6.624 \times 10^{-27}) (2.998 \times 10^{10}) / 6.1 \times 10^{-12} \\ = 3.3 \times 10^{-5} = 330 \text{ nm}$$

This value is in good agreement with¹⁴⁴ with the experimental value of 313 nm.

As another case, let us discuss a specific dye, 1,1 – diethylcyanineiodide (cryptocyanine): Figure 1.22. The cation can resonate between two limiting structures, which really means that the wave function for the ion has equal contribution from both the states. Thus all the bonds along this chain can be considered as equivalent, with bond order of 1.5 similar to the C— C bond in benzene. Each carbon atom in the chain and each nitrogen atom in the ends are here involved in bonding with three atoms by three localized bonds, the so-called sigma bonds. The extra valence electrons on the carbon atoms in the chain and the remaining three electrons on the two nitrogen atoms form a mobile cloud of pi electrons along the chain and extend above and below the plane of the chain. We then assume that the potential energy is constant along the chain and that it rises sharply to infinity at the ends; that is the pi electron system is replaceable by free elections moving in a one dimensional box of length L, and for example, if it is supposed that total number of pi electrons in this system be N, then as said before, for electron transition and consequent light absorption, the transition energy and the wavelength of maximum absorption can be arrived at as in equation E .2 and E.3 respectively. To reproduce the latter,

$$\lambda = 8mcL^2 / h(N + 1)$$

E.3

The number of carbon atoms in polymethine chain, if suppose, are p , then $N = p + 3$. Kuhn assumed that the length of the chain between nitrogen atoms plus one bond distance on each side; thus, $L = (p + 3)l$ where l is the bond length between atoms along the chain. Therefore,

$$\lambda = 8mcL^2(p + 3)^2 / h(p + 4)$$

E.4

Putting $l = 1.39 \times 10^{-8}$ cm (the bond length of benzene, a molecule with similar bonding) and converting from centimeters to nanometers (1 nm = 10^{-9} m), we find,

$$\lambda \text{ (in nm)} = 63.7(p + 3)^2 / (p + 4)$$

E.5

If there are easily polarizable groups at the ends of the chain, such as benzene rings, the potential energy of the pi electrons in the chain does not rise so sharply at the ends. In effect, this lengthens the path L , and we can write,

$$\lambda \text{ (in nm)} = 63.7(p + 3 + \alpha)^2 / (p + 4)$$

E.6

where α should be constant for a series of dyes of a given type. If such a series is studied experimentally, this empirical, α , may be adjusted to achieve the best fit the data; in any event, should lie between 0 and 1¹⁴⁵

In order to compare the results of this method with the more sophisticated Valence Bond (VB) or the molecular (MO) calculations, let us use equation 5 which assumes that $\alpha = 0$, to calculate the wave length of maximum absorption of cryptocyanine, in which $p = 9$ and compare that value with those given by others in the literature¹⁴⁶:

Free electron	= 707 nm
Bond orbital (case 1)	= 3900 nm
Bond orbital (case 2)	= 2900 nm
Molecular orbital	= 2700 nm

It may be noted that only FEM predicts an absorption band in the visible region of the spectrum in agreement with the actual observation. Kuhn has applied this method to the determination of the wavelength of maximum absorption of a number of cyanine dyes with varying values of α , whose classical structures are presented in figure XVI. Both the structures are equivalent. The potential energy of the well of the model is not, however, constant due to the presence of two nitrogen atoms. The number of atoms in the conjugated chain is $2a + 9$ and since the potential energy barrier extends beyond the terminal nuclei by about one bond length, the number of pi electrons N is $2a + 10$. Each carbon atom contributes one electron and the two terminal atoms together contribute three electrons. Since the C—C bond distance is known, the total length, L , of the well can be calculated. The individual bond distance is taken as 1.39×10^{-8} cm, i. e. the C—C bond distance in the benzene molecule. Table 2 summarizes the calculated values of λ_{\max} , which are in good agreement with the experimental values obtained by Brooker¹⁴⁷ over the range where a , the number of vinyl groups, increases from zero to three.

TABLE 2
Positions of absorption bands in the spectra of cynine dyes

A	a	λ_{\max} (calc.) ¹⁴⁸ nm	λ_{\max} (observed) ¹⁴⁷ nm
0		579	590
1		706	710
2		834	820
3		959	930

The agreement is good considering that the terminal benzene rings are not included in the calculations. By using linear compound similar cyanine dyes in structure, but not containing benzene rings, i. e. those of the general structure,



where the value of a is 1, 2, or 3, Simpson¹⁴⁹ has found excellent agreement between observed and the calculated values of λ_{\max} . The total number of pi electrons is $(2a + 4)$ including again a contribution of three electrons from the nitrogen atoms. With a reasonable estimate of the length of the potential well, values of λ_{\max} shown in table 3 were obtained.

TABLE 3

Position of absorption bands in the spectra of cyanine analogues

A	a	Calculated λ_{\max} nm	Observed λ_{\max} nm
1		309	309
2		409	409
3		509	511

Let us consider a symmetrical cyanine dye with m conjugated double bonds in the resonating chain connecting the two nitrogen atoms. The number of pi electrons in the chain amounts to $2m + 2$, and the absorption band corresponds to a jump of electron from the HOMO level $m + 1$ to the LUM level $m + 2$. As before the energy for this transition is:

$$\Delta E = h^2(m_e + 2)^2 / 8m_e L^2 - h^2(m + 1)^2 / 8m_e L^2 = h^2(2m + 3) / 8m_e L^2 \text{ and}$$

$$\lambda_{\max} = hc / \Delta E = 8m_e c / h \times L^2 / (2m + 3) \quad \text{Equation 7}$$

This remarkable result in this approximation indicates that the position of the absorption band is determined by the chain length and by the number of pi electrons $2m + 2$, since m_e , the mass, h , the Planck's constants and c , the velocity

of light are universal constants. Further λ_{\max} does not depend upon any specific property of the atoms along the chain. The length L may be taken as equal to $2m \times l$ where l is bond length of the chain elements; the average bond length, l , has been taken as 1.3 angstrom on the basis of approximations considered by Kuhn¹⁵⁰⁻⁵¹. The electron gas stretches by length, αL , on the both sides of the each terminal nitrogen atom. Thus, a more satisfactory value of L is given by

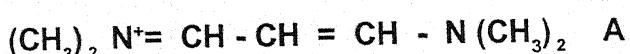
$$L = 2m \times l + 2\alpha \times l = 2l \times (m + \alpha)$$

Now according to equation 7

$$\begin{aligned} \lambda_{\max} &= 8m_e c / h \times 4l^2 (m + \alpha)^2 (2m + 3) \\ &= 127 (m + \alpha/2)^2 / (m + 3/2) \text{ nm} \end{aligned} \quad \text{Equation 8}$$

In the conjugated polyenes, symmetrical cyanines and their analogues, Kuhn¹⁵² has calculated the stretching of the electron gas to both sides of each terminal atom, as 1.5 angstroms, on the basis of vibrational treatment. As the length αl on both the ends is approximately 1.5 Å this may be considered that $\alpha = 1$. The value $\alpha = 1$ has already been used in the treatment of the dye molecule, Figure 1.24. It has been found that the value of α is dependent on the end groups, and thus in a homologous series of dyes α is constant for all the members of the series. If strongly polarizable groups in increasing order are introduced in the terminal atoms, the value of α also increases. On the basis of above considerations the calculated value of λ_{\max} of the said dye with $m = 2, 3, 4, 5, 6$, and 7 are in excellent agreement with experimental data¹⁵³ of these carbocyanines.

The free electron method has also been used¹⁵⁴ to determine longest wavelength of absorption of a number of basic dyes and to compare the influence of a central nitrogen atom in a conjugated system. In the simplest case the linear compound A is compared with the aza derivative B in which the central carbon atom has been replaced by nitrogen. This atom contributes one electron to the total pi system and since it is more electronegative than carbon atom that it replaces, there will be decrease in the HOMO energy level in the ground state.



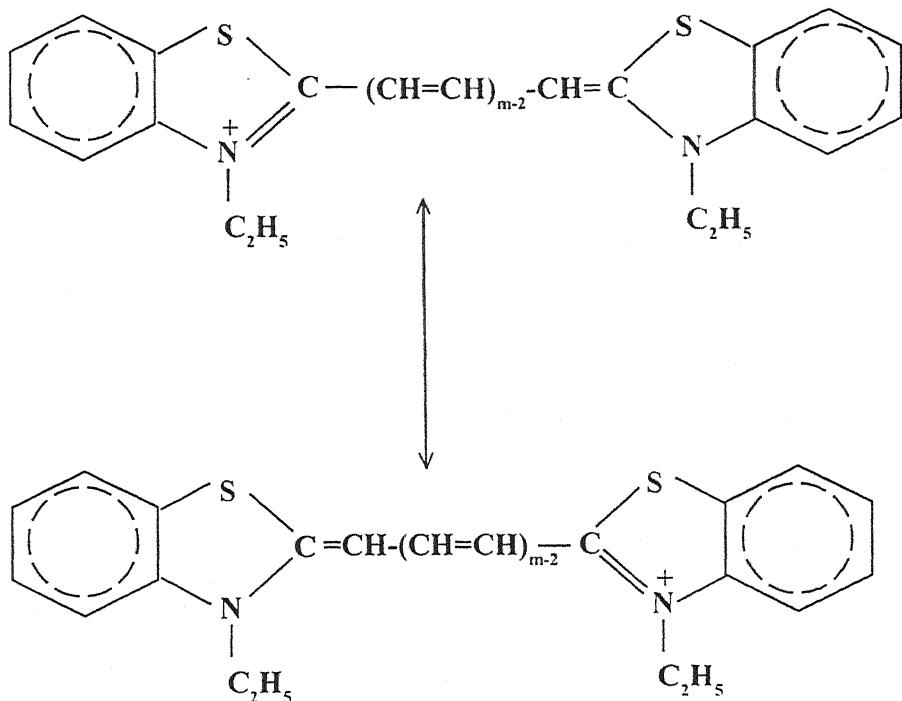


FIGURE 1.24

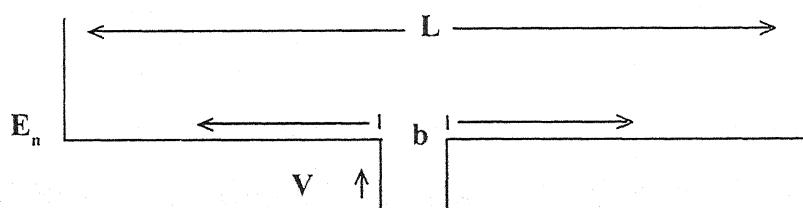


FIGURE 1.25

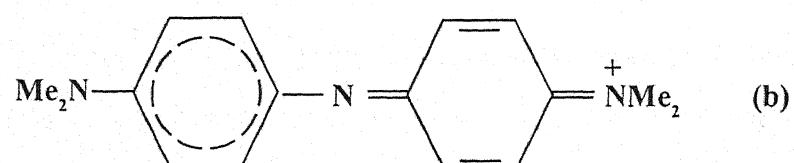
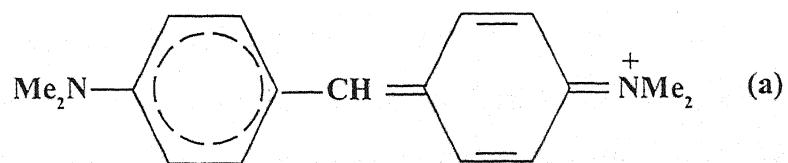


FIGURE 1.26



In the first excited state of both A and B, there is vibrational node at the central atom and the energy level in both the cases is equivalent. Consequently the excitation energy ΔE involved in the transition will be greater for aza derivative, which therefore possesses λ_{\max} at a shorter wavelength. In general, when centrally situated $-\text{CH} =$ group is replaced by $-\text{N} =$ in a resonating system between terminal nitrogen atoms, a hypsochromic shift is observed if there is an even number of double bonds and a bathochromic shift is seen when the number of double bonds is odd. This is because the value of the energy levels in the excited state depends on presence of a node or an anti node at the central atom.

The displacement of a given energy level caused by the nitrogen substitution may be quantitatively assessed by a perturbation treatment and is given by the equation

$$\epsilon = -A\psi^2 \quad \text{Equation 9}$$

where A is an electronegativity constant, characteristic of the heteroatom and is equal to 3.9×10^{-20} erg cm for the $-\text{N} =$ atom, ϵ is the normalized wave function at the heteroatom. It can be shown that $2/L$ give the square of the normalized wave function, where L is again the length of the potential well. It follows that for a state with an anti node at the central atom

$$\epsilon = -Ax^2/L = -2A/2(M+\alpha)l \quad \text{Equation 10}$$

where M is the number of double bonds and l is the mean carbon-carbon bond distance. The factor α is introduced, as said before, to account for the extension of constant well potential beyond the terminal atoms of the conjugated system. The potential well diagram of the simplified free electron model is modified by the presence of electronegative atom to that shown in figure 1.25.

The nitrogen atom is situated at the center of the well and where b, the mean C-N distance, is small compared to the total well length, the probability of finding electron in the trough is $\psi^2 b$. The reduction, ϵ , in the total energy of the state n is, therefore, $-V\psi^2 b$ where V is the negative potential due to the nitrogen atom. It

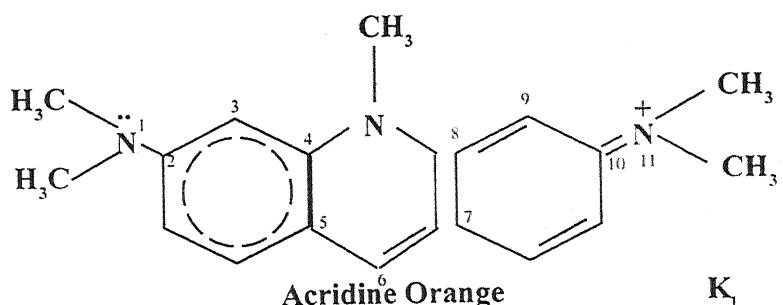


FIGURE 1.27

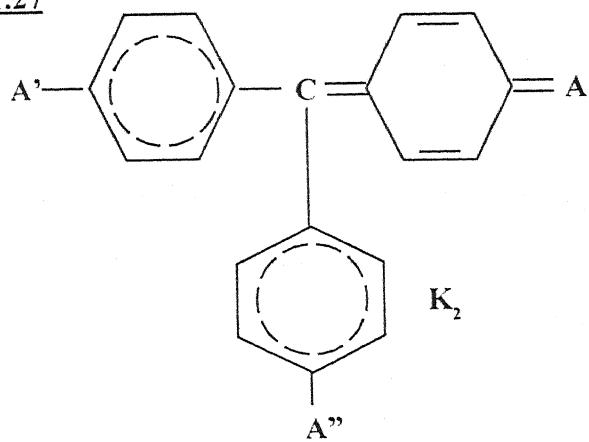
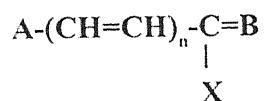


FIGURE 1.28a

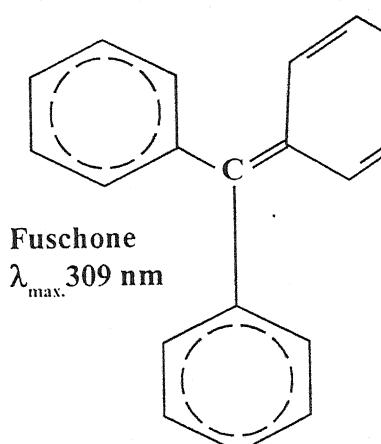


FIGURE 1.29

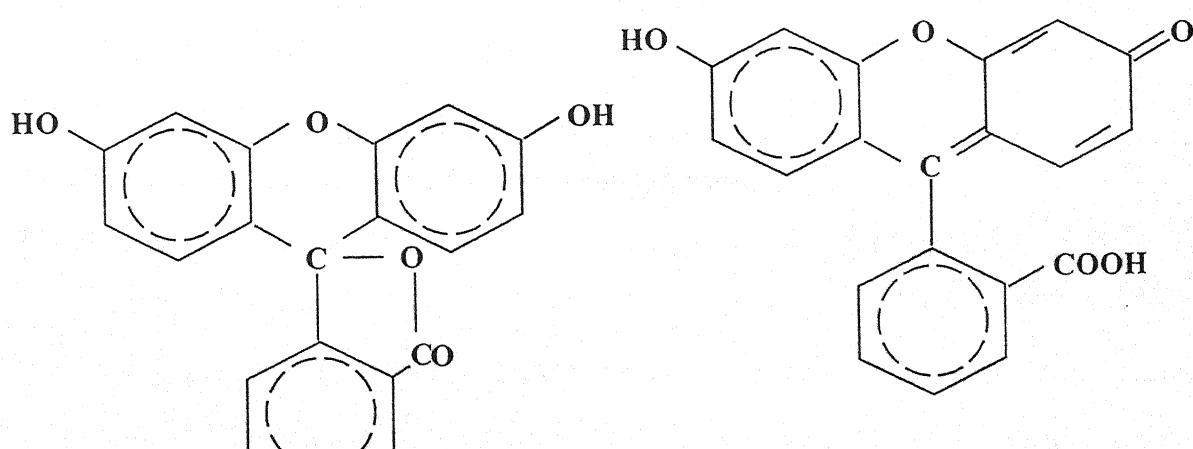


FIGURE 1.31

FIGURE 1.30

Fluorescein

$\lambda_{\text{max}} 495$

follows from equation 9 that $A = Vb$ or in other words the electronegativity constant is the product of the potential energy drop and the bond distance between the hetero atom and its neighbour.

A comparison of the spectra of Michler's Hydrol Blue and Bindschedler's Green, the structures of which are shown in figure 1.26a and 1.26b, shows that the observed value of λ_{max} are 603 and 725 nm respectively. If the $\Delta E'$ is the excitation energy of the aza dye, then,

$$\Delta E' = \Delta E + \varepsilon \quad \text{Equation 11}$$

for the excited state possessing a central antinode the $\Delta E'$ is the excitation energy of the parent unsubstituted molecule (a) in the said figure and

$$\begin{aligned} E &= hc/\lambda_{max} = 6.62 \times 10^{-27} \times 3.00 \times 10^{10} / 6.03 \times 10^{-5} \\ &= 3.30 \times 10^{-12} \text{ erg,} \end{aligned}$$

equation 11 can be calculated from equation 10 since the values of all the constants, with the exception of α , are known. This factor α may be determined by calculating the value of L when observed value of λ_{max} for the parent molecule is substituted in equation 3. Comparison of this value of L with the value calculated from the number of double bonds and the mean bond length, as shown by Kuhn¹⁵⁴, gives $\alpha = 0.55$. The number of double bonds is five and from equation 10,

$$\begin{aligned} \varepsilon &= -(3.9 \times 10^{-20}) / (5 + 0.55) (1.39 \times 10^{-8}) \\ &= -0.5 \times 10^{-12} \text{ erg} \end{aligned}$$

The values of $\Delta E'$ is the sum of these energy terms.

$$\begin{aligned} \Delta E' &= 3.30 \times 10^{-12} - 0.5 \times 10^{-12} \\ &= 2.80 \times 10^{-12} \text{ erg.} \end{aligned}$$

Expressing this energy in wave length terms gives a wave length of maximum absorption for Bindschedler's Green (figure 1.26b) at 709 nm, a calculated shift of 106 nm, in reasonable agreement with the observed shift of 122 nm on replacing the central - CH = group by - N = group. Similarly, Michler's Hydrol Blue may be compared with Acridine Orange, figure 1.27.

The electronegativity constant for A for $N - CH_3$ at the position 12 in this compound is 6.0×10^{-20} erg cm. In the normal state of the molecule the seven pairs of pi electrons, contributed from the five double bonds and uncharged nitrogen atoms, fill the seven highest occupied energy levels. A free electron model treatment as above gives a calculated value of λ_{max} for acridine orange of 471 nm compared with an observed value of 491 nm. The absorption spectra of acridine, oxazine, thiazine, azine and xanthene dyes have all been compared by this method¹⁵⁴ with some degree of success.

Equation 3 predicts that the absorption band with the lowest energy should be displaced to longer wavelengths when an increasing number of ethylenic linkages is introduced into the molecule since L^2 is proportional to the wave length. However, with linear polymers, the wave length of absorption tends to a maximum as the number of double bonds is increased. The assumption of a constant pi electron potential in the simple free electron model has been shown¹⁵⁵ to be incorrect and a regular variation in bond length occurs along the chain if it is sufficiently long. Such a varying energy along the box increases the gap between the occupied and the unoccupied orbitals so that λ_{max} tends to limit as the chain length increases. In terms of resonance theory explanation is that in long chains of this type, the number of idealized structures contributing to the stability of the excited state increases to a greater extent than the contribution each makes to the stability of the ground state. Consequently, the energy differences increase with the increasing chain length.

The FEMO theory has certain features in common with the qualitative interpretation of the special shifts associated with Burawoy's K - band theory¹⁵⁶ in triarylmethane dyes and thiobenzophenone derivatives¹⁵⁷, particularly in its application to the basic dyes, where the electronegative atom situated in a conjugated system can act as an electron sink. The intense K - bands (Burawoy's nomenclature - K - konjugierte) are attributed to $\pi \longrightarrow \pi^*$ excitation when a conjugated molecule contains both an electron donating and electron withdrawing group, a shift of the

K – band to a longer wave length occurs which is greater than the additive effect of both groups when acting separately. Changes in the nature of the terminal groups in such systems which cause an increase in polarity or polarizability, or the dissolution of the compound in more polar solvents, cause further shift of the K – bands to the longer wavelengths. The presence of the side chain groups also effects the position of the K – band, opposing the electron migration from terminal groups, e. g. from A to B in figure 1.27a, where A and B may be $N(CH_3)_2$ and $=N^+(CH_3)_2$ respectively and assisting it in the new system of groups X (which may be, e. g. $-OH$ or $-NH_2$) and group B. This replacement of K-band is, therefore, to shorter wave lengths with thiobenzene and triarylmethane cations which are symmetrically substituted, the side chain is also conjugated. The absorption spectra show only one band but should in fact consist of two superimposed bands, i. e. originating from K_1 and K_2 in figure 1.28b

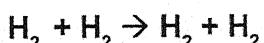
These bands become apparent when the absorption spectra of non-symmetrically triarylmethane chromophores are examined. When A, A' and A'' are identical and are either $-CH_3$, $-SCH_3$ or $-NCH_3$, (Crystal violet) then only one band is observed at 480, 577 and 587 nm respectively. Replacement of one substituents in each of these compounds by hydrogen, (e.g. changing crystal violet to malachite green) causes the emergence of a second band K_2 at shorter wave lengths. Simultaneously, the K_1 - band undergoes a bathochromic shift of between 20 and 40 nm. Similar observations have also been made by Lewis and Bigeleisen¹⁵⁸ for Crystal Violet and the sodium salts of Rhodamine B and Fluorescein.

Kuhn has used the branched pi electron gas model to treat other dyes in a similar manner and the concept of branching leads to a simple explanation of even such characteristic compounds as the deep colour of the low molecular weight Wurster's Blue and azulene¹⁵⁹.

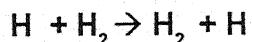
It of interest to consider the application of the free electron theory to closed ring systems having conjugation similar to that occurring in porphyrins, azaporphines and phthalocyanines. The free electron theory has been applied to the metal free

porphins¹⁶⁰, cyclic polyynes¹⁶¹ and phthalocyanines¹⁶²⁻⁶³, using a circular box model, and by taking into account the perturbation factor calculated from atomic shielding constants¹⁶⁴, better agreement¹⁶⁵ has been found with the experimental data¹⁶⁶. Labhart¹⁶⁷ further refined the free electron theory by taking into account the interaction between the pi electrons and the elastic sigma skeleton. He showed that even for very long polyynes a difference in single and double bond length was of the same order of magnitude as in shorter polyynes was to be expected. Olszewski¹⁶⁸ used a linear free electron model with electron – electron and electron – core interaction for the calculation of lowest excited singlet-triplet separation in polyynes, twisting frequency of ethylenes and location of absorption maxima in cumulenes. He also calculated the absorption maxima in the spectra of symmetrical cyanine dyes and polyenes by ASFEMO (Anti – Symmetrical Free Electron Molecular Orbital) method. An improvement of the theoretical λ_{\max} values for cyanines was obtained by introducing resonance barrier¹⁶⁹ in the free electron model. Spectra of cyanine dyes and cata – condensed hydrocarbons were analysed by Araki and Huzinaga¹⁷⁰⁻⁷¹, Basu¹⁷², Dey¹⁷³ and by Rout et al.¹⁷⁴ who applied suitably modified FEMO method.

Apart from spectral analysis, the refined FEMO has also been used for the calculation of optical rotatory power¹⁷⁵ of the organic molecule. The model gave a method for rapid evaluation of electric and magnetic transition moments and was further used for a better understanding of the skew conformation of butadiene. Schuler¹⁷⁶ used the free electron model for calculating the stability constants and absorption spectra of pi molecular complexes. Mueller¹⁷⁷ examined theoretically the bimolecular exchange reaction



and



via activated complex by free electron model. Bonham et al.¹⁷⁸ and Basu¹⁷⁹ treated the electrophilic substitution in aromatic molecules by the FEMO method. The treatment is based on the fact that any aromatic substitution reaction proceeds

through the formation of the activated complex. Nathan¹⁸⁰ successfully employed the FEMO method for theoretical investigation of diamagnetism of aromatic hydrocarbons.

1.4.7 TWO DIMENSIONAL FREE ELECTRON GAS MODEL:

The two-dimensional free electron gas model¹⁸³ is similar to the branched electron gas model, which has been described earlier in this chapter itself. Each state of interest in a two dimensional model corresponds to a stage in the one-dimensional model. In the two-dimensional model with a system of canonical forms, the plane at the centre of the atoms is chosen as the xy plane of the xyz co-ordinate system. It is assumed that the pi electrons are in the potential field $V(z) + V(xy)$ where $V(z)$ is a certain function of z . $V(xy)$ is the potential of the pi electron averaged over z and is a sum of the contributions of the carbon atoms. The contribution of the carbon atom can be obtained by the nuclear charge and shielding considerations. The z part of the wave function of the electron in the potential $V(z) + V(xy)$ can be separated from the xy part and the problem of finding eigen functions $\phi_n(xy)$ and eigen values E_n of the Schrodinger wave equation

$$\delta^2\psi_n/\delta x^2 + \delta^2\psi_n/\delta y^2 + 8p^2 [E_n - V(x,y)] \psi_n/h^2 = 0$$

using an analog computer.

The two-dimensional method can be applied to polyenes and polyacetylenes. Using the observed values of bond distances, the position of the strong absorption bands was calculated and the results were in good agreement with those of the one-dimensional treatment and also with the experimental data¹⁸⁴.

1.5 PHTHALEINS: THEIR COLOUR AND CONSTITUTION

Figures 1.30, 1.31 and 1.32 depict the phthalein dyes that constitute an entirely different series. These dyes may be obtained by simply replacing $N - CH_3$ by more electronegative oxygen atom at the position 12 and H at position 6 by C_6H_5COO in acridine orange (figure 1.27). These phthaleins are derivatives of pyronines and may be considered to be intermediates between fuscon (figure 1.29) and bezaurine (figure 1.32).

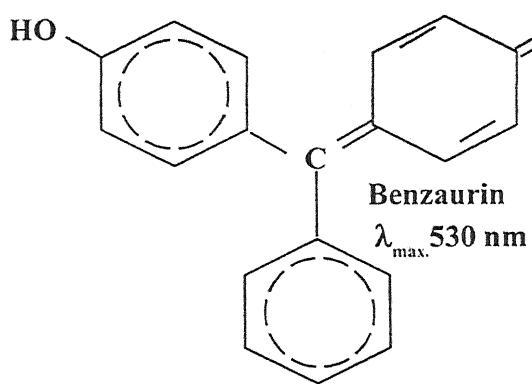


FIGURE 1.32

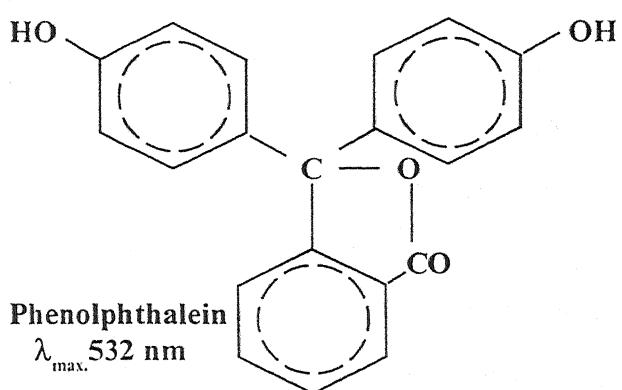


FIGURE 1.33

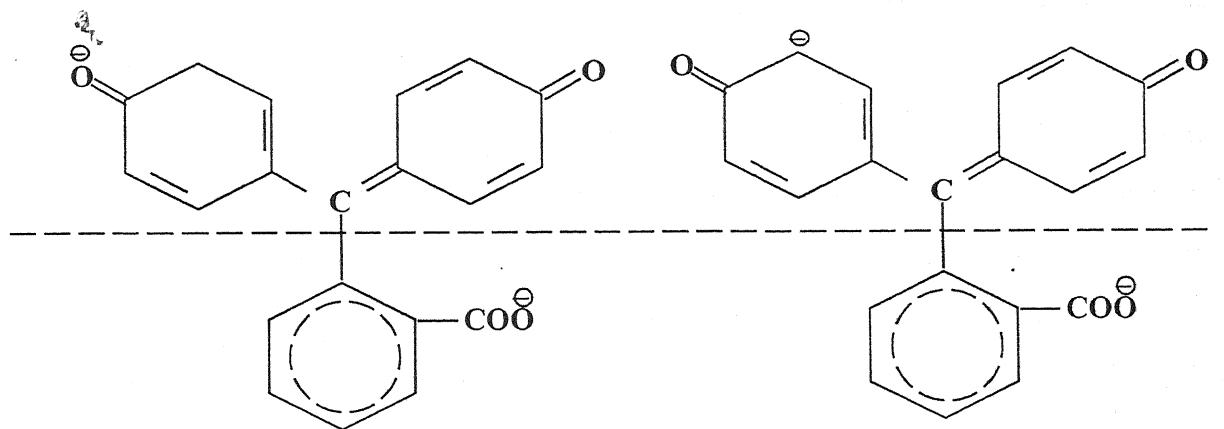


FIGURE 1.34

FIGURE 1.35

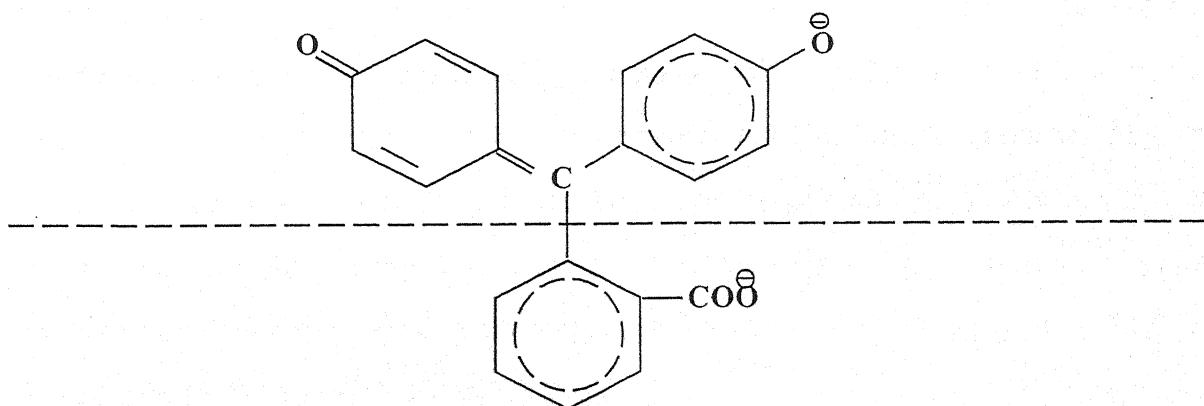


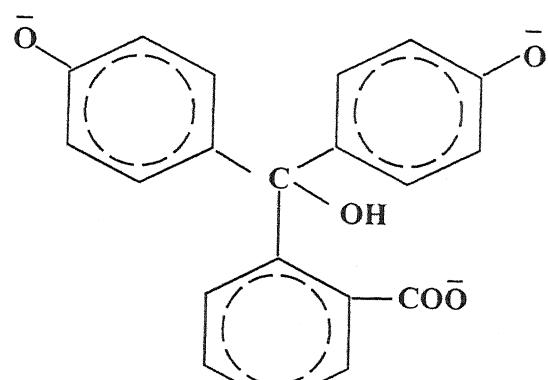
FIGURE 1.36

The colour in these phthalein dyes is attributable to the anionic portion which is thus the more important part of the molecules. This series of dyes have been established to bear a lactone structure in neutral medium are thus colourless (figure 1.33). In alkaline solutions (pH 8.4) these dyes undergo ring opening producing intense red divalent anions (figure 1.34). They produce the longest wavelength at band $\lambda_{\text{max.}}$ at 532 nm with an extinction coefficient of 31000. The well known property of phenolphthalein as an indicator is due to this very intense red divalent anionic form which is a hybrid of structures shown in the figures 1.34 and 1.36 and a number of its possible resonating structures. The divalent anion transforms to carbinol (figure 1.30) a trivalent anion, when excess alkali is added, and thus loses the colour.

Fluorescien (figure 1.30) is an analogue phenolphthalein in that it differs in only the presence of an oxygen bridge. Both phenolphthalein and fluorescien in alkaline medium exhibit bathochromic shift. In each case, the alkali produces an ion that can be represented by two equivalent resonating structures. Thus the alkali produces ions that are stabilised by resonance and this leads to the absorption at longer wavelengths. Fluorescien has two equivalent canonical forms depicted in figures 1.38a and 1.38b in the alkaline medium.

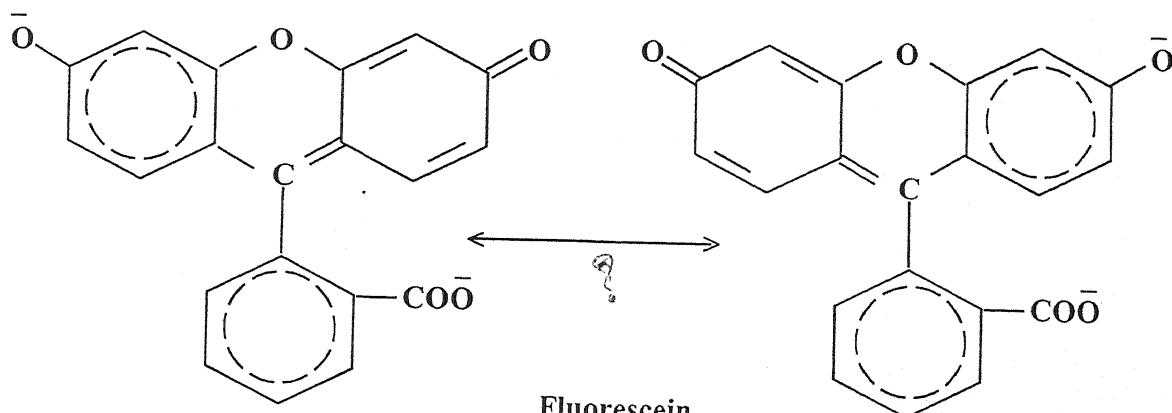
Fluorescien expectedly absorbs at shorter wavelength as compared to phenolphthalein. The fluorescien ion is red ($\lambda_{\text{max.}}$ in water 500 nm) whereas the phenolphthalein ion is magenta ($\lambda_{\text{max.}}$ in water 550 nm). Fluorescien absorbs at shorter wavelength because in it the charge distribution between two oxygen atoms is decreased due to the oxygen bridge of the pyrone ring which is capable of forming a double bond with the ring acquiring some of the available charge. Fluorescien is characterised by strong green fluorescence and many of derivatives have been found to exhibit the property.

Eosin (Figure 1.39) having some bromine atoms at ortho position to pyrone



Trivalent anion (a carbinol derivative)

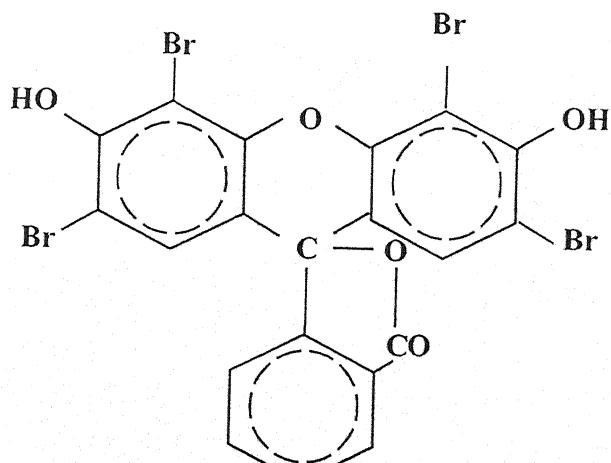
FIGURE 1.37



Fluorescein

FIGURE 1.38a

FIGURE 1.38b



Eosin

FIGURE 1.39

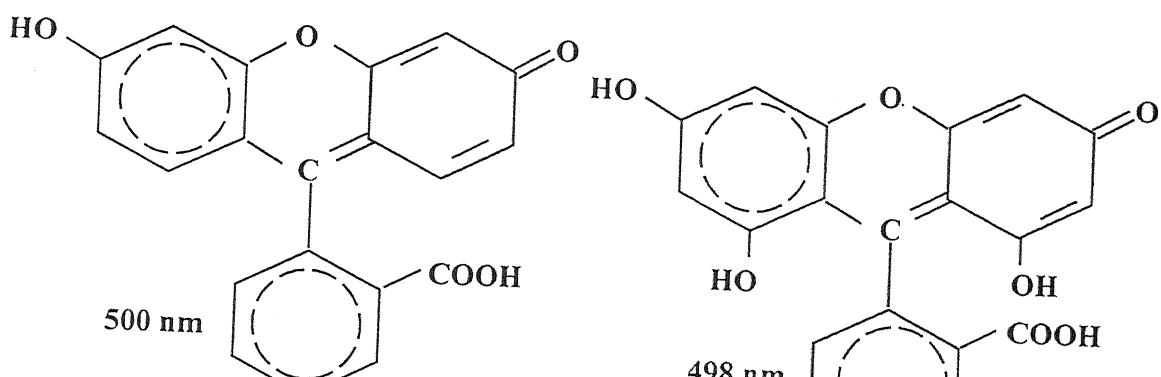


FIGURE 1.40

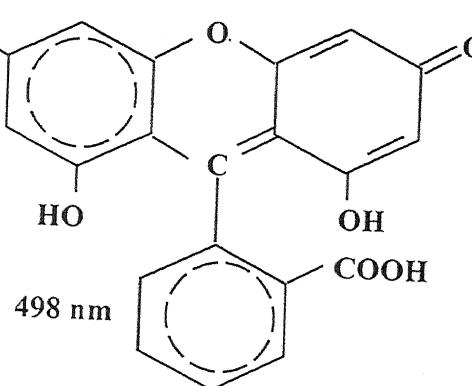


FIGURE 1.41

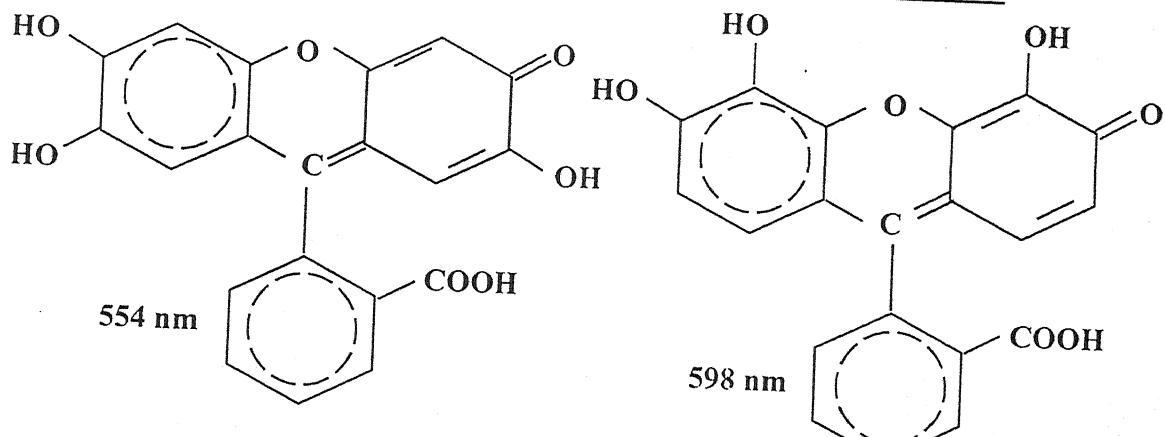


FIGURE 1.42

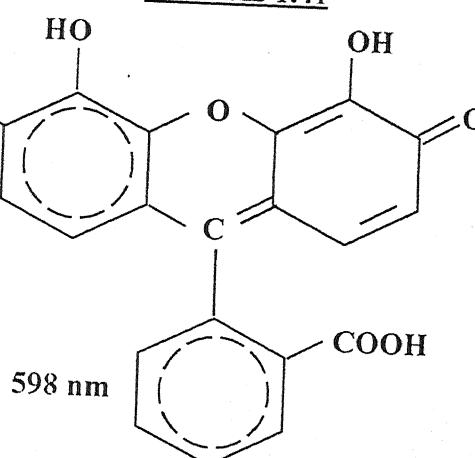


FIGURE 1.43

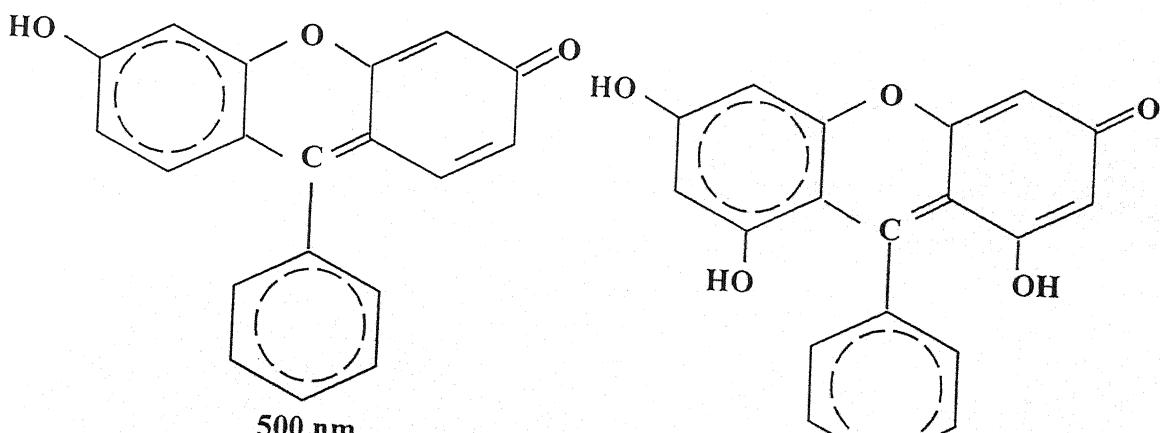


FIGURE 1.44

FIGURE 1.45

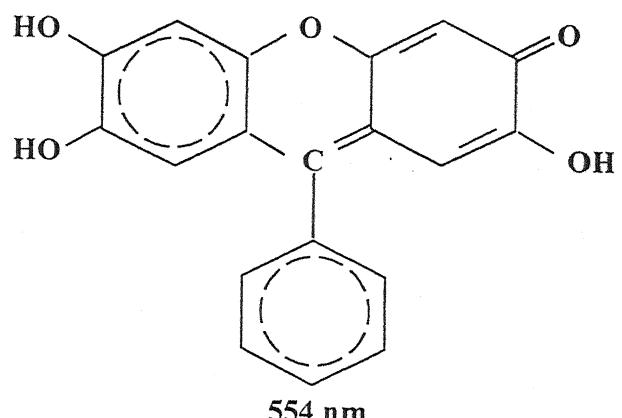


FIGURE 1.46

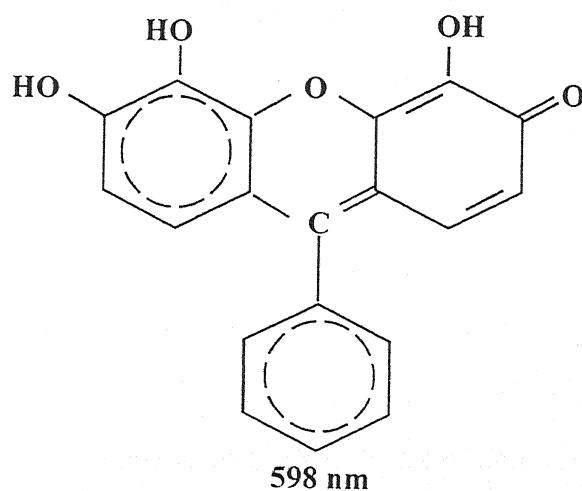
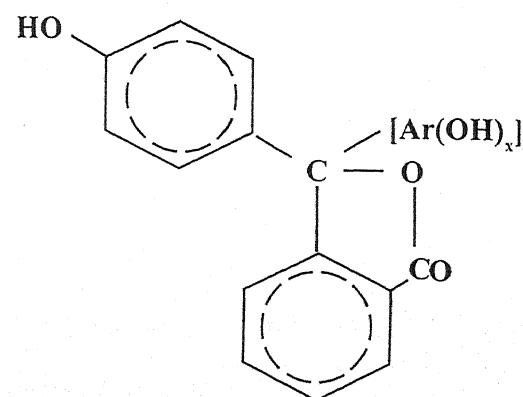
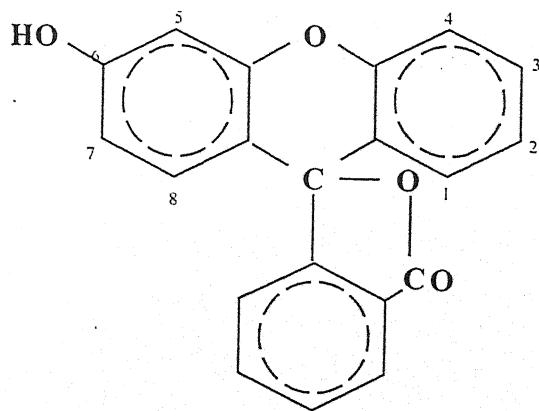


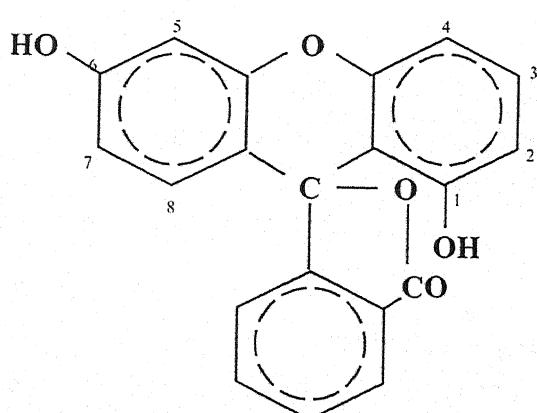
FIGURE 1.47



Phthalophenone derivatives
FIGURE 1.48



6-hydroxyfluoran
FIGURE 1.49



1,6-hydroxyfluoran
FIGURE 1.50

oxygen, electron density at carbon atom of pyrone is increased and consequently it hinders oxygen to take part of the oscillating charge. It is evident from the structure of phthalein (figure 1.34 and 1.36) and also from the above considerations that only the part of the molecule which is shown above the dotted line plays an important part in the light absorption as regards the main absorption band of the molecule is concerned. The removal of the carboxyl group in the compounds, figures 1.40 to 1.43, does not affect the position of the absorption maxima in compounds shown in figures 1.44 to 1.47. A number of workers¹⁸⁵⁻²⁰⁵ have studied the effect on light absorption in compound depicted in figures 1.30 to 1.33 and could find no significant changes in λ_{\max} which confirm the previous observations. Ghatak and Dutt²⁰⁶ have prepared phthaleins of the type, figure 1.48, in which two hydroxy molecules are dissimilar. They also prepared asymmetric fluorosceins where the substituents in the two sides of fluoran nucleus are not identical as shown in figures 1.49 and 1.50. So what?

In the recent times, Beg and coworkers²⁰⁷⁻²¹¹ have prepared and studied some novel analogues of phthalein and succinein dyes with special emphasis on the synthesis and colour aspects. The present investigations are in continuation of the work that has already been done by these researchers.

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CHAPTER

TWO

RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSION

2.0 INTRODUCTION

The detailed discussion in Chapter I makes it amply clear that if any change is to be made in frequency of the first transition band, it is not worthwhile to modify the acid part in the resonance of the dye molecule. Instead, the alteration in number of auxochromes, their position in the resonating part of the molecule has considerable influence on the magnitude of λ_{\max} . The lactone form of phenolphthalein in alkaline medium can be represented by two equivalent quinonoid forms Figure 1.34 and Figure 1.36. Obviously we can create a situation that would result in drastic alteration in the molecule by the replacement of one of the hydroxy group aromatic nuclei by an alkyl group or an aryl group or by a heterocyclic ring. Then resonance in the phenolphthalein ring becomes possible on the two quinonoid forms mentioned above. The colour development of the modified form is expected to be much less intense than in the case of phenolphthalein. In order to investigate effect of alterations in the non acid upper part of the molecules of the phthalein molecules as discussed in the previous lines, thirteen γ -keto acids in four series A, B, C and D were prepared and condensed with various phenolic compounds to obtain novel asymmetric phthaleins or more correctly called phthal-as-eins. The general structure of phthal-as-eins is represented by figure 2.01.

2.1 SERIES OF γ -KETO ACIDS EMPLOYED

Acids of series A

1. 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid
2. 2-(5'-chloro-2'-methylbenzoyl) benzoic acid
3. 2-(3'-chloro-4'- chloromethylbenzoyl) benzoic acid

ACIDS OF SERIES B

1. 2-(2'-hydroxy-5'-methylbenzoyl) terachlorobenzoic acid
2. 2-(5'-chloro-2'- methylbenzoyl) terachlorobenzoic acid

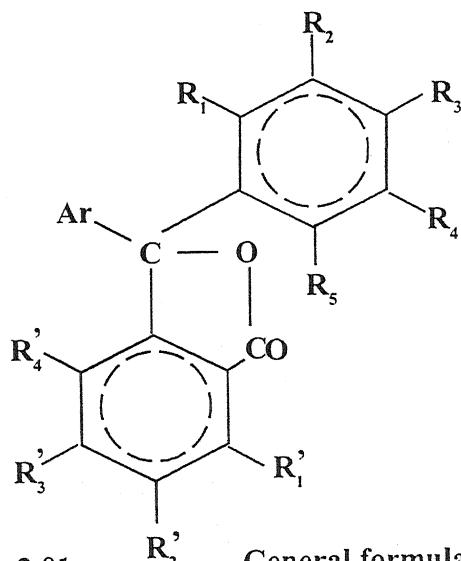
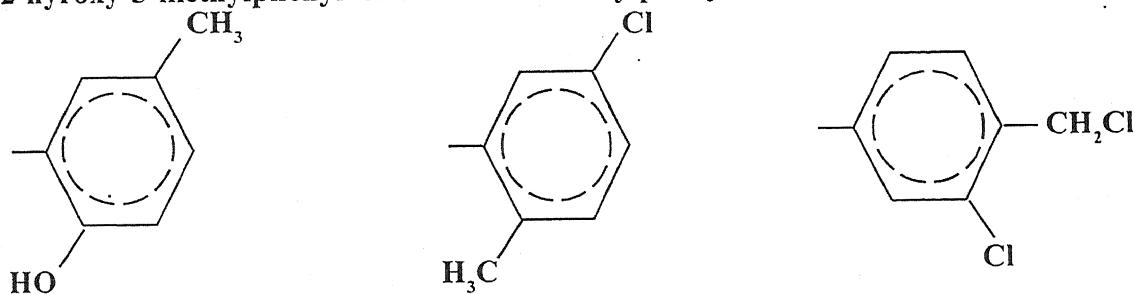


Figure 2.01 General formula of a phthal-as-ein

For dyes Derived from A, B and C, Ar =

2-hydroxy-5-methylphenyl or 5-chloro-2-methylphenyl or 3-chloro-4-chloromethylphenyl



$R_1 = R_2 = R_3 = R_4 = R_5 = H$ or OH ; $R_2 = R_4 = H$ or Br

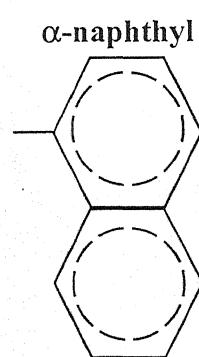
$R_1 = R_3 = OOC-CH_3$

$R_1' = R_2' = R_3' = R_4' = H$ (for dyes derived from series A)

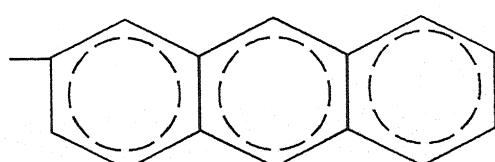
$R_1' = R_2' = R_3' = R_4' = Cl$ (for dyes derived from series B)

$R_1' = R_2' = R_3' = H$; $R_4' = NO_2$ (for dyes derived from series C and D)

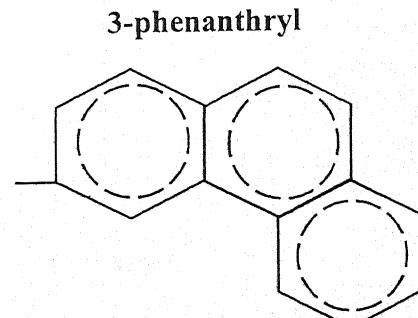
For dyes derived from series D, Ar =



α -naphthyl

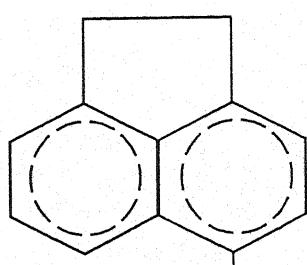


2-anthracyl



3-phenanthryl

and 3-acenaphthoyl



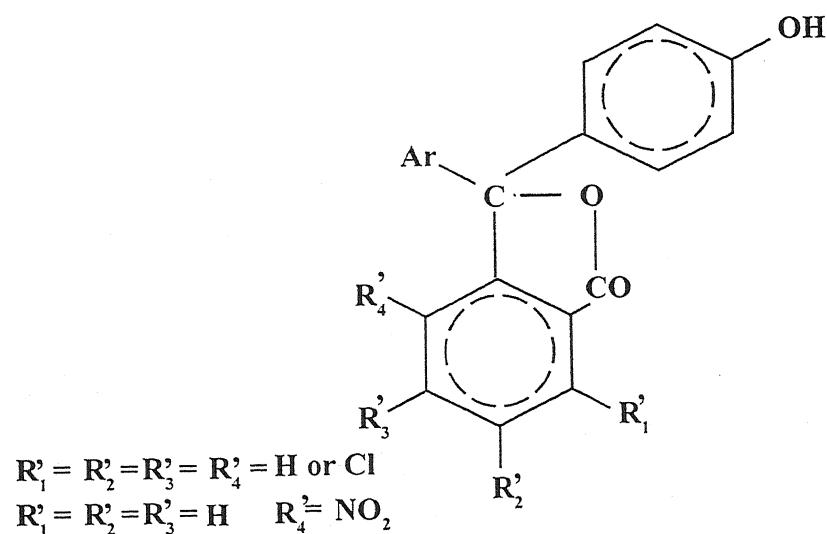


Figure 2.02

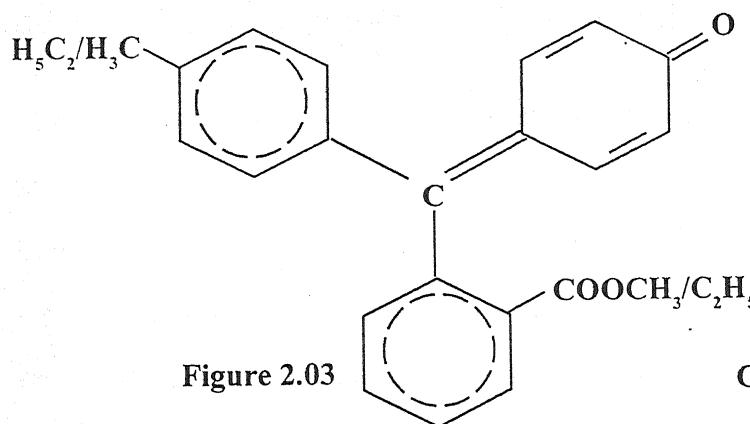


Figure 2.03

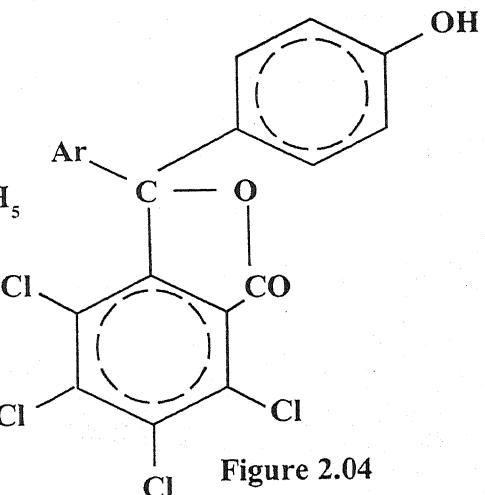


Figure 2.04

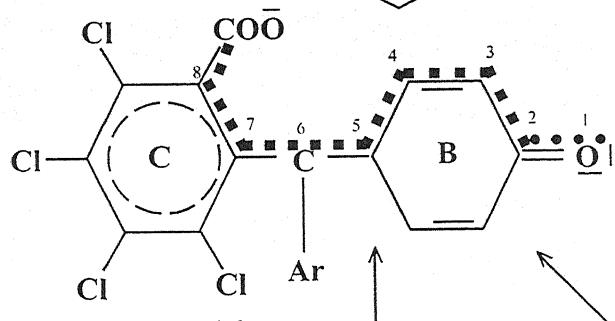


Figure 2.06

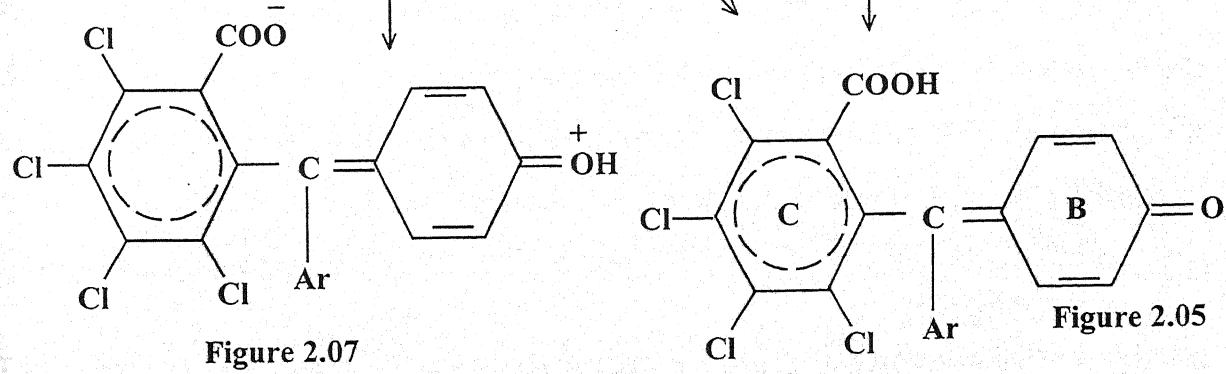


Figure 2.07

Figure 2.05

3. 2-(3'- chloro-4'- chloromethylbenzoyl) terachlorobenzoic acid

ACIDS OF SERIES C

- 1 2-(2'- hydroxy- 5'- methylbenzoyl)- 3 nitrobenzoic acid
- 2 2-(5'-chloro-2'- methylbenzoyl) -3 nitrobenzoic acid
- 3 2-(3'- chloro-4'- chloromethylbenzoyl) - 3 -nitrobenzoic acid

ACIDS OF SERIES D

1. 2-(α -naphthoyl)- 3 – nitrobenzoic acid
2. 2 – (2' – anthracenoyl) - 3 – nitrobenzoic acid
3. 2 – (3' - phenanthroyl) - 3 – nitrobenzoic acid
4. 2 – (3' – acenaphthoyl) - 3 – nitrobenzoic acid

The asymmetry in the structure of the molecules has been taken into consideration for their nomenclature. These molecules can be safely considered to be mixed or unsymmetrical phthaleins shown in Figure 2.01 as derivatives of phthalide. For the sake of convenience and uniformity and due to the presence of asymmetric carbon atom present in all of them, the more satisfactory nomenclature for structure in Figure 2.01 has been adopted.

2.2 STRUCTURE OF PHTHAL-AS-EINS:

Chemical investigation into the constitution of such dyes (figure 2.01) as discussed in the previous subsection have been assigned the structure as depicted in figure 2.02 to the family of phenol-phthal-as-eins.

The phenol-phthal-as-ein assigned the structure in figure 2.02 is noticeably similar to dimethyl¹⁻² and diethyl derivative (figure 2.03) of phenolphthalein. In these derivatives, there seems the possibility of the same type of resonance as is postulated for phenolphthalein itself. Similarly, the resonance of phenolphthalein type will be altogether absent in figure 2.02.

Thus, the analogue of the dimethyl derivative is orange red and the corresponding

derivative is yellow even in the solid state.

The representative dyes of the four series are enumerated below:

SERIES A:

1. (2-hydroxy-5-methylphenyl) phenol-phthal-as-ein
2. (5-chloro-2- methylphenyl) phenol-phthal-as-ein
3. (3-chloro-4-chloro- methylphenyl) phenol-phthal-as-ein

These three dyes are brown, dark brown and reddish brown respectively.

SERIES B:

1. (2-hydroxy-5-methylphenyl) phenol tetrachloro phthal-as-ein
2. (5-chloro-2- methylphenyl) phenol tetrachloro phthal-as-ein
3. (3-chloro-4-chloro- methylphenyl) phenol tetrachloro phthal-as-ein

The above three dyes are pale rosy, pinkish white and rosy respectively.

Series C:

1. (2-hydroxy-5-methylphenyl) phenol nitro phthal-as-ein
2. (5-chloro-2- methylphenyl) phenol nitro phthal-as-ein
3. (3-chloro-4-chloro- methylphenyl) phenol nitro phthal-as-ein

The above three dyes are pinkish red, light pink and light pink respectively.

Series D:

1. α -naphthyl phenol nitro phthal-as-ein
2. 2- anthracenyl phenol nitro phthal-as-ein
3. 3-phenanthryl phenol nitro phthal-as-ein
4. 3- acenaphthyl phenol nitro phthal-as-ein

These four dyes are leaf brown, brown, gulf red and leaf green respectively.

The colour of these phenol phthal-as-eins in neutral as well as alkaline medium and

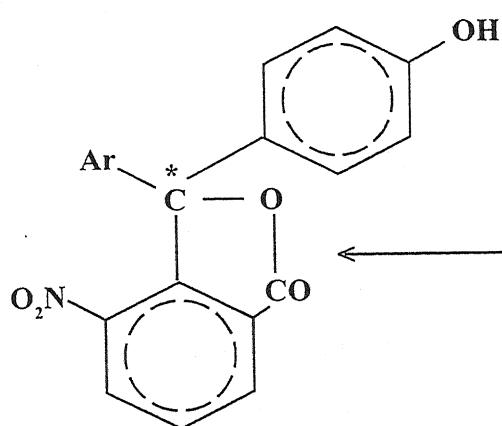


Figure 2.08

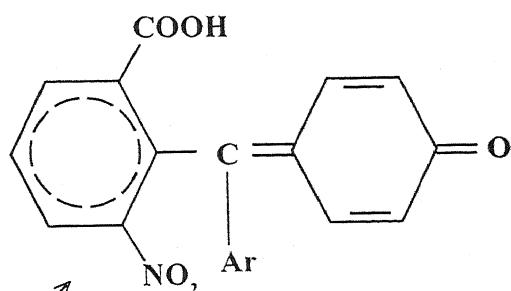


Figure 2.09

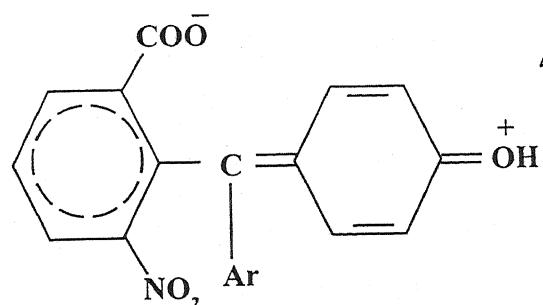


Figure 2.10

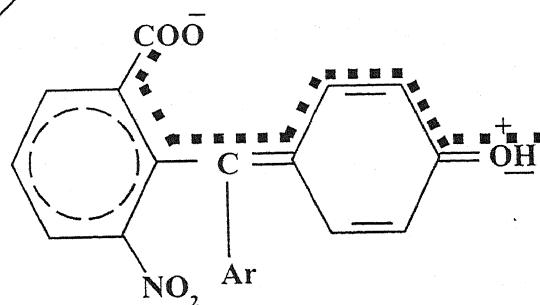
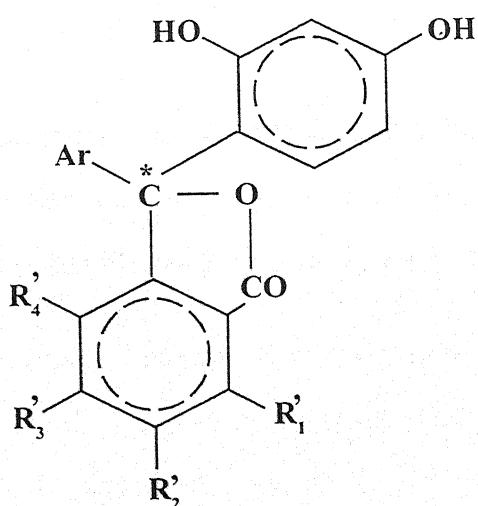


Figure 2.11



Resorcinol phthal-as-ein

Figure 2.12

$\text{Ar} = (2\text{-hydroxy-5-methylphenyl})$;
 $(5\text{-chloro-2-methylphenyl})$;
 $(3\text{-chloro-4-chloromethylphenyl})$;
 $(\alpha\text{-naphthyl})$;
 (2-anthracenyl) ;
 (3-phenanthryl) ;
 (3-acenaphthyl)

$\text{R}'_1 = \text{R}'_2 = \text{R}'_3 = \text{R}'_4 = \text{H} = \text{Cl}$

$\text{R}'_1 = \text{R}'_2 = \text{R}'_3 = \text{H} ; \text{R}'_4 = \text{NO}_2$

their λ_{\max} values are presented in tables placed toward the end of this thesis. The colour of all these thirteen dyes may be rationalized on the basis of theories and interpretations presented in the previous chapter.

The colour of phenol tetrachloro phthal-as-eins may be interpreted on the basis of resonance that takes place among the neutral structures 2.04 and 2.05 and polar structures 2.06 and 2.07 structures of the dye molecules. As a result of resonance taking place in the molecule, the quinonoidal conjugation becomes a reality in the various participating structures while simultaneously a formal charge is created in the polar resonating states in the alkaline medium. The symmetry of phenolphthalein is altogether absent but perhaps, the charge travels through the dotted line (figure 2.07) and the absorption maxima coincides with that of phenolphthalein. The phenol tetrachloro phthal-as-eins investigated by us display a similar behavior in basic medium as phenolphthalein. The monovalent anion of phenolphthalein is a colourless derivative, while the divalent anion (figure 1.34 to 1.36) tends to yield pink colour but the trivalent anion like the monovalent one is colourless (figure 1.37). Similarly, the phenol tetrachloro phthal-as-eins described in the thesis give pink colour in moderate basic medium and the disodium salts are almost colourless. The divalent colourless anion with strong acids shows again an increase in the intensity of colour (figure 2.06).

In the same manner the colour of the phenol nitro phthal-as-eins under investigation can also be explained by considering the neutral (figure 2.028 and figure 2.09) and the polar (figure 2.10 and figure 2.11) canonical forms of the dye molecules.

The colour of the resorcinol phthal-as-eins (figure 2.12) may be explained in the context of their chemical structures discussed in the previous section as in the case of phenol phthal-as-eins.

In resorcinol phthal-as-eins, there are two hydroxy groups at 2 and 4 positions instead of one hydroxy group at 4 position in the hydroxy aromatic part of the molecule

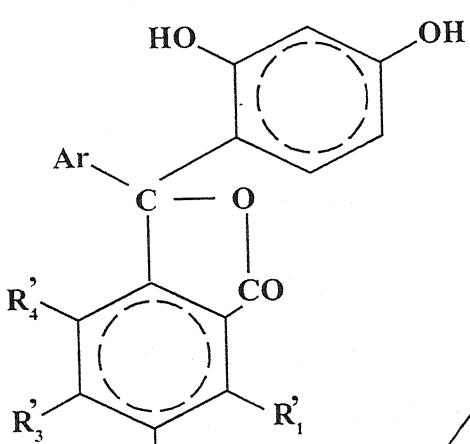


Figure 2.12

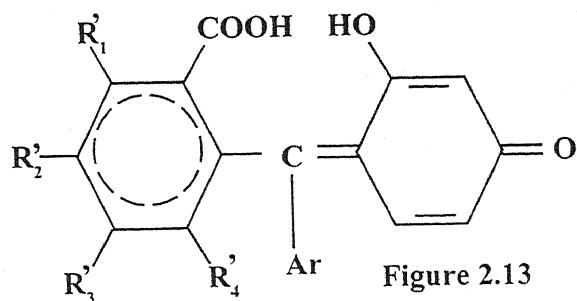


Figure 2.13

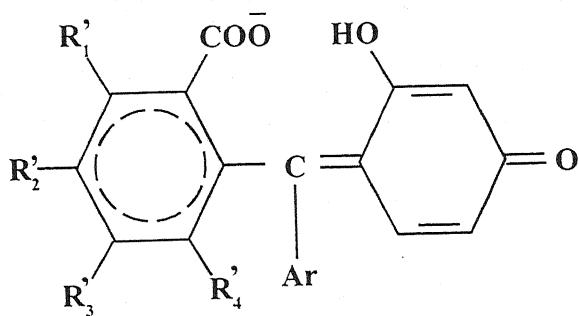


Figure 2.13a

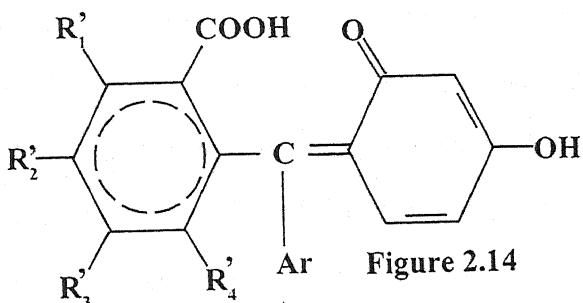


Figure 2.14

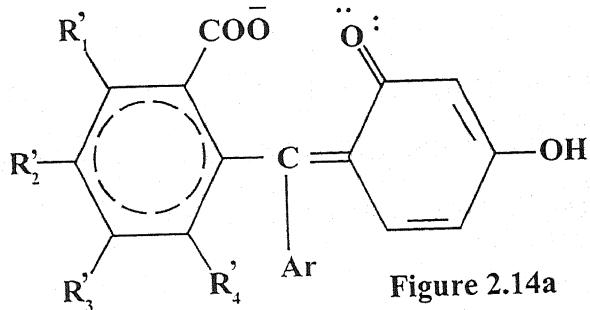


Figure 2.14a

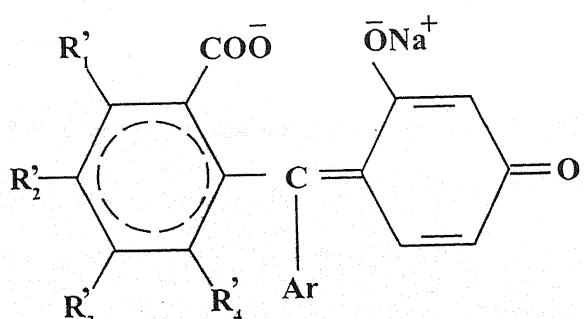


Figure 2.13b

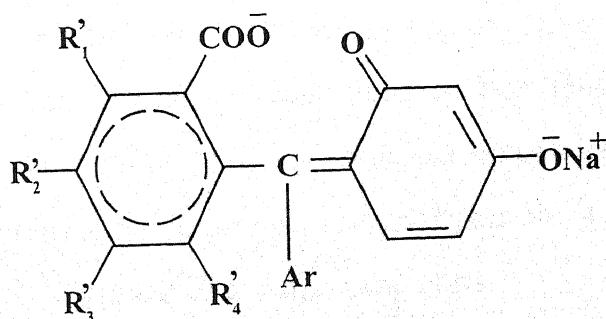


Figure 2.14b

(figure 2.12). Out of the two hydroxy groups. One acts as a chromophore to provide conjugation while the other hydroxy group acts as an auxochrome. Consequently, even a neutral molecule can exist as a resonance hybrid of the figure 2.12 to figure 2.14 molecular structures.

We can therefore safely conclude that the colour of resorcinol phthal-as-eins can be rationalized either in the solid state ((yellow, yellowish orange, yellowish brown) and in neutral medium (λ_{\max} 460-485 nm). But in the alkaline medium, the polar forms of the molecule (figure 2.13a, figure 2.14a, figure 2.13b and figure 2.14b) of the molecule become available in solution so that the number of resonating structures of the molecules increases. As a result, more crowded and depressed energy levels are produced i.e. a bathochromic shift occurs. As a matter of fact all these dyes yield absorption band at 460-485 nm in neutral medium. However in slightly alkaline medium the λ_{\max} are shifted to the range of 490-520 nm.

It has been observed that in a very large number of polyhydroxy phenol phthal-as-eins, one hydroxy group acts as a chromophore and the remaining ones as auxochromes to cause a deepening of colour of the dyes (varying from yellow to brown). In some cases these dyes e.g. hydroquinone, catechol, phloroglucinol and pyrogallol phthal-as-eins have been found to decompose in the alkaline medium. Due to this decomposition of dyes, reliable absorption maxima can not be experimentally found. One can not therefore offer an adequate interpretation of their colour.

Thus one can safely conclude that no single theory can adequately explain and predict the colour of all types of dyes with a fairly satisfactory accuracy and precision. However, FEMO gas model fits the bill better than all the other theories that have been put forward to explain and predict colour of the dyes. All the theories such as VB, MO and FEMO require rigorous assumptions. Otherwise it would just not be possible to apply the computations for even simplest of the dye molecules.

2.3 COLOUR OF PHTHAL-AS-EIN DYES: CALCULATION OF ABSORPTION

MAXIMA:

Rigorous approximations must have to be made to determine the theoretical values of absorption maxima of phenol phthal-as-eins as per the π gas model as in equation 3 in the previous chapter. In the dyes under investigation, each dye molecule is unsymmetrical. Consequently, two equivalent extreme structures with formal charges for molecules like that of phenolphthalein or fluorescein are not possible. Under the circumstances unsymmetrical extended conjugated chains with formal charge at one end may be present in all the canonical forms to represent the actual dye molecule. In order to compute λ_{\max} major structures like figure 2.07 and figure 2.13a are taken into consideration. In these structures in all ten electrons are required to take part in the π electron gas; eight electrons of four π bonds and two electrons from the charge of free OI (neutral oxygen atom). The effective conjugated chains have been depicted by dotted line and for simplification, the lower portion is neglected by making approximations that do not materially affect the results. Thus, a polar five π -electron gas cloud is possible which is responsible for the creation of coulombic force along the polar molecule with formal charge. To consider the stretching beyond the two ends of the conjugated chain, it is possible only at one end, which is the OI end. The value of $\alpha = 0.33$ has been calculated from the experimental λ_{\max} value for the benzaurine dye XXV of the first chapter with oxygen end groups. The application of equation of equation 8, we get,

$$\begin{aligned}\lambda_{\max} &= 127(m + \alpha/2)^2 / (m + 3/2) \text{ nm} \\ &= 127(5 + 0.33/2)^2 / (5 + 3/2) \text{ nm} \\ &= 127(5.165)^2 / 6.5 \text{ nm} \\ &= 520 \text{ nm.}\end{aligned}$$

This value is in good agreement with the experimental values obtained for phenol

phthal-as-eins (530-560 nm) and resorcinol phthal-as-eins (530 – 560 nm).

It has not been possible to apply the free electron molecular orbital treatment in the case of polyhydroxy phenol phthal-as-eins due to unmanageable difficulties presented by their structural complexities to arrive at a simple equation for determination of their absorption maxima.

4. It may be worthwhile to point here that H. Kuhan³⁻⁴ have made the provision of a refined treatment on the basis of "one dimensional wave shape potential Model" which is applicable for completely symmetrical type of the dye molecules. The same author has proposed a still better treatment on the basis of "two dimensional electron gas model"⁵ and it is claimed that this may be applied to dye molecules of any complicated shape. But it involves tedious mathematical calculations, which discourages most investigators. The various phenol phthal-as-eins prepared e. g. (2-hydroxy-5-methylphenyl) phenol-phthal-as-ein, (5-chloro-2-methylphenyl) phenol-phthal-as-ein and (3-chloro-4-chloro- methylphenyl) phenol-phthal-as-ein are brown, black, and dark brown respectively. The bathochromic shift is quite significant in these phenol-phthal-as-eins in the alkaline medium. Their λ_{\max} values in neutral and in alkaline medium are 520- 540, 510 – 530 and 500 – 520 nm respectively.
4. The colours and the λ_{\max} values of the dyes (2-hydroxy-5-methylphenyl) phenol tetrachloro phthal-as-ein, (5-chloro-2- methylphenyl) phenol tetrachloro phthal-as-ein (3-chloro-4-chloro- methylphenyl) phenol tetrachloro phthal-as-ein, (2-hydroxy-5-methylphenyl) phenol nitro phthal-as-ein, (5-chloro-2- methylphenyl) phenol nitro phthal-as-ein, (3-chloro-4-chloro- methylphenyl) phenol nitro phthal-as-ein, α -naphthyl phenol nitro phthal-as-ein, 2- anthracenyl phenol nitro phthal-as-ein, 3-phenanthryl phenol nitro phthal-as-ein, 3- acenaphthyl phenol nitro phthal-as-ein are pink(λ_{\max} 530-535 nm), pink (λ_{\max} 520-530 nm), pinkish white (λ_{\max} 530 nm), brown (λ_{\max} 500-530 nm), light red (λ_{\max} 520 nm), black (λ_{\max} 510-530 nm), brown (λ_{\max} 500-530 nm), light red (λ_{\max} 520 nm), black (λ_{\max} 510-530 nm), brown

(λ_{\max} 530 nm), pale yellow (λ_{\max} 510-530 nm), light brown (λ_{\max} 530 nm), and (λ_{\max} 510 nm) respectively.

These dyes are colourless in neutral medium and in basic medium give violet, rose red, violet, pinkish red, pink, violet, pink, pinkish red, pink and pink respectively. The above λ_{\max} values observed have been found to be in good agreement with the λ_{\max} values of analogous phenol phthal-as-eins.

1. Phenol phthal-as-eins, λ_{\max} , 550 nm in alkaline medium
2. Phenol tetrachloro phthal-as-eins, λ_{\max} , 580 nm in alkaline medium
3. Phenol nitro phthal-as-eins, λ_{\max} , 560 nm in alkaline medium

The higher λ_{\max} values observed for phenol tetrachloro phthal-as-eins and phenol nitro phthal-as-eins may be attributed to the presence of auxochromes in the phenyl ring. These groups may be held responsible for the enhancement of colour. The presence of nitro group in the acid part in phenol nitro phthal-as-eins may be partly responsible for the enhancement of λ_{\max} values and the colour of the dyes.

In various resorcinol phthal-as-ein dyes prepared the λ_{\max} (460-480 nm) in neutral and 490-520 nm in alkaline medium is lower than the λ_{\max} values observed in various phenol phthal-as-eins. It may be possibly explained by the fact that in resorcinol phthal-as-eins LVI there are two hydroxy groups at 2:4 positions instead of only one group at 4 position as in phenol phthal-as-ein dye structure XLVI. Thus, in one of the main contributing structures of the molecule, conjugation is blocked beyond the 2-hydroxy group LVIIa and as a result the length of the conjugated chain is reduced. This decrease in length of the conjugated chain LVIIa may be held responsible for lowering of the λ_{\max} values of these compounds.

All the resorcinol phthal-as-eins, under investigation, have absorption maxima at 460-480 nm in the neutral medium and 490-520 nm in moderate alkaline medium. The values of absorption maxima for these resorcinol phthal-as-ein dyes have been presented in a tabular form at the end of this treatise.

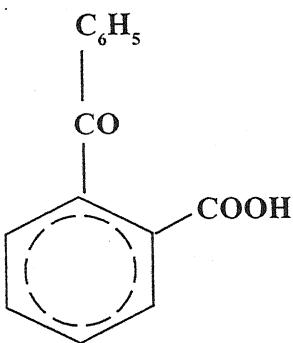


Figure 2.15

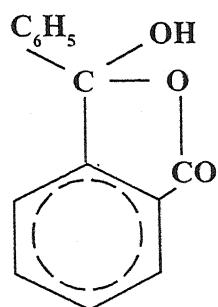


Figure 2.16

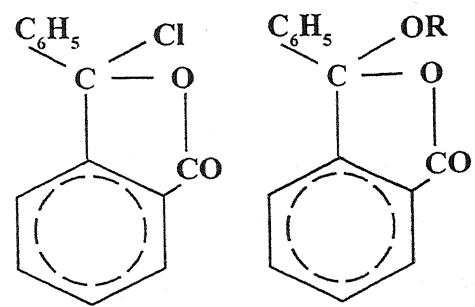


Figure 2.17

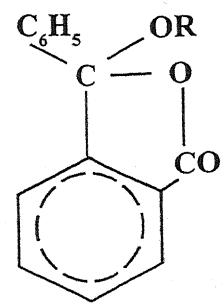


Figure 2.18

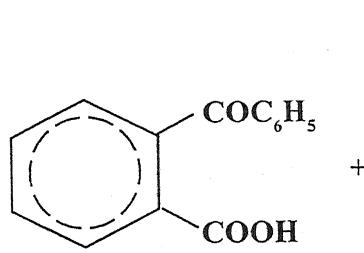


Figure 2.15

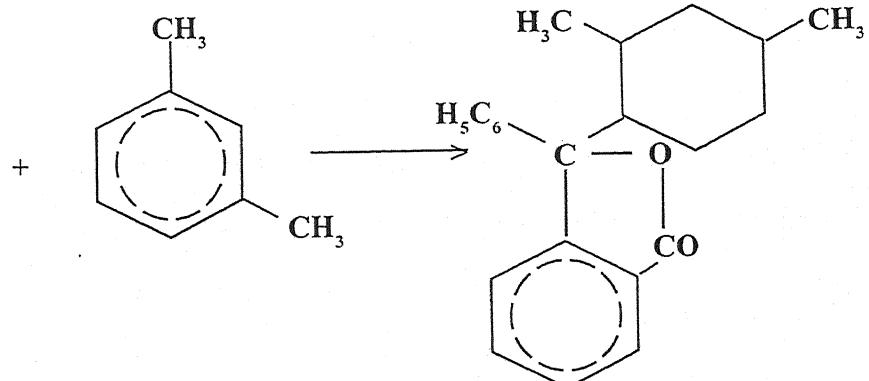


Figure 2.19

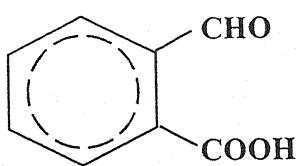


Figure 2.20

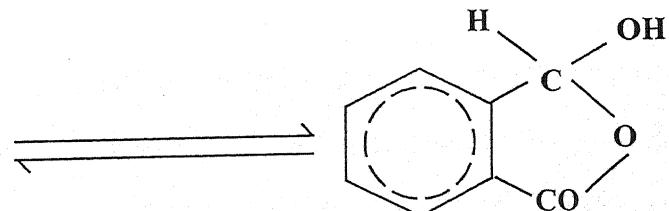


Figure 2.21

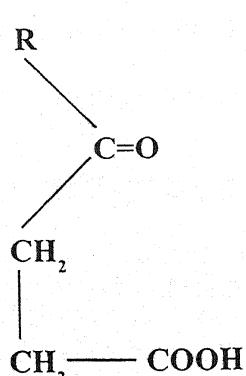


Figure 2.22

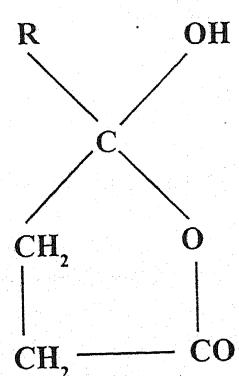


Figure 2.23

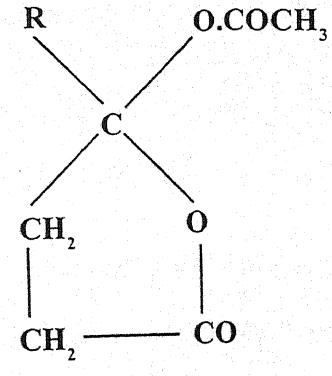


Figure 2.24

We have made the following crucial observations during the course of investigation of these dyes:

1. A significant difference between the phthalein dyes (pyronine dyes) and phthal-as-ein dyes reported in the thesis are clearly discernible. While considering the different charged structures to explain their respective colour or to calculate the theoretical value of, in the first case the acid part is not considered at all while in the second case the acid part is involved and is capable of producing a number of charged structures which may be held responsible for their colour.
2. There is very little effect of difference in substituents in the aromatic ring of the acid part but it may be noted that the phthalein dyes derived from γ -keto acids having 2-hydroxy-5-methyl, 5-chloro-2-methylphenyl and 3-chloro-4-chlormethylphenyl substituted in the lactol carbon (central carbon atom) show a little more bathochromic shift. It might be due to these very substituents mentioned above. The substitution of α -naphthyl, 2-anthracenyl, 3-phenanthryl and 3-acenaphthyl substituents at lactol carbon has practically no impact on the λ_{\max} values.
3. Though no single theory is capable of explaining and predicting the colour and the absorption maxima of all types. However the FEMO gas model is best equipped presently available to solve our problem of calculating and predicting the colour and the absorption maxima after making some assumptions which do not have any significant effect. In the present work FEMO gas model has been employed to successfully calculate the λ_{\max} values that are in excellent agreement with the experimental values.

2.4 CHEMICAL CONSTITUTION OF PHTHAL-AS-EIN DYES:

The open chain substituted or unsubstituted γ -keto acids possess a characteristic structural requirement due to which they are capable of existing in cyclic tautomeric forms too. The formation of the ring tautomer (lactol form) takes place due to electrophilic ring chain tautomerism where the electrophile is the proton (hydrogen).

Amount of lactol depends on the extent of prototropic change. Generally, it has been observed that the γ -keto acids exist chiefly as lactol or equilibrium mixture of ring and chain isomers⁷⁻⁸. The lactols give well-defined crystalline acetyl derivatives, still retaining their cyclic structures. Therefore, it is obvious that cyclic tautomer is comparatively more stable form than the chain isomeric form⁹⁻¹². The formation of pseudoesters¹³ of o-benzoyl benzoic acid LIX has been proposed on the basis of cyclisation of lactol LX that can yield a pseudochloride¹⁴. This pseudochloride, on heating with an appropriate alcohol, yields the corresponding ester figure 2.18.

Formation of compound figure 2.19 from o-benzoyl benzoic acid and metaxylene catalysed by perchloric acid has been proposed through the 3-phenyl phthalyl carbonium ion, where the precursor of this carbonium ion is definitely the cyclic isomer¹⁵⁻¹⁶ (figure 2.16) of o-benzoyl benzoic acid.

The formation of lactol intermediate has also been used to explain some of the other chemical reactions of o-benzoyl benzoic acid e. g. the reductive coupling¹⁷ of the acid with phosphorous and hydroiodic acid. The cyclic structures for pseudoesters have been confirmed by IR¹⁸ and Raman¹⁹ spectra.

o-acetylbenzoic acid has been shown to yield acetyl derivative through the formation of lactol⁹ intermediate as in the case of o-benzoyl benzoic acid. Peculiarly enough, o-acetyl bezoyl chloride behaves a bit abnormally from the chemical point of view. All attempts to convert o-acetyl benzoyl chloride to o-acetyl benzaldehyde have failed, by the Rosenmund reduction or any other reaction. It also can not be converted into o-diacetyl benzene²⁰. Its conversion to amides with amines has also resulted in failure or very nominal yield²¹. This abnormal chemical behaviour of o-acetyl bezoyl chloride is actually to be expected, if one considers that acid chloride prepared in each case with thionyl chloride, is undoubtedly cyclic and ring tautomeric acid chlorides invariably lead to cyclic products rather than those attempted in the above synthetic attempts. The lactol formation has been further confirmed by IR²² and NMR²³

spectral studies. In the recent years it has been reported that the acid in liquid form exists chiefly in the lactol form²⁴.

The formation of pseudoesters as well as a large number of other alkyl derivatives²⁵²⁶ of phthal-aldehydic acid (figure 2.20) can be explained by considering the lactol form (figure 2.21) of the acid. NMR spectra of phthal-aldehydic acid and o-acetylbenzoic acid indicate that the acids exist in cyclic forms²⁷. IR spectra of phthal-aldehydic acid show bands at 3322 cm^{-1} , 1755 cm^{-1} and 1745 cm^{-1} which support the presence of the acid chiefly in the lactol form.

Open chain γ -keto acids viz. Laevulinic acid or β -acetyl propionic acid (figure 2.22, $R = \text{CH}_3$) and β -benzoyl propionic acid (figure 2.22, $R = \text{C}_6\text{H}_5$) have also been reported to exist in their tautomeric lactol form as shown in figure 2.23.

These two γ -keto acids form acetyl derivatives^{12,13} (figure 2.24) that is possible through their lactol form only. On account of display of such chemical behaviour, laevulinic acid has been shown to be a mixture of ring and chain isomers^{7,8}. It has been noted that ring tautomerism²⁷ is further increased by changing R to a larger alkyl group or aryl group and is further enhanced by change of α -hydrogen atom to the carboxylic groups to larger alkyl group or α - β -ethylenic linkage²⁸. In all such cases, the cyclic form has been found to predominate in solution.

2.5 IR SPECTROSCOPIC EXAMINATION OF γ -KETO ACIDS AND THEIR ACETYL DERIVATIVES:

Thirteen γ -keto acids listed earlier in the chapter belonging to four different series viz. A, B, C and D have been used for the preparation of dyes in the work presented in this dissertation. IR spectral examination of these acids clearly reveals their natural existence as mixture of ring and chain tautomers. There are typical peaks displaying the presence of diarylketonic $> \text{C}=\text{O}$ ($1675 - 1700\text{ cm}^{-1}$), carboxylic $> \text{C}=\text{O}$ ($1695 - 1710\text{ cm}^{-1}$), lactonic $> \text{C}=\text{O}$ ($1735 - 1790\text{ cm}^{-1}$), carboxylic - OH ($2600 - 2700\text{ cm}^{-1}$) and lactol

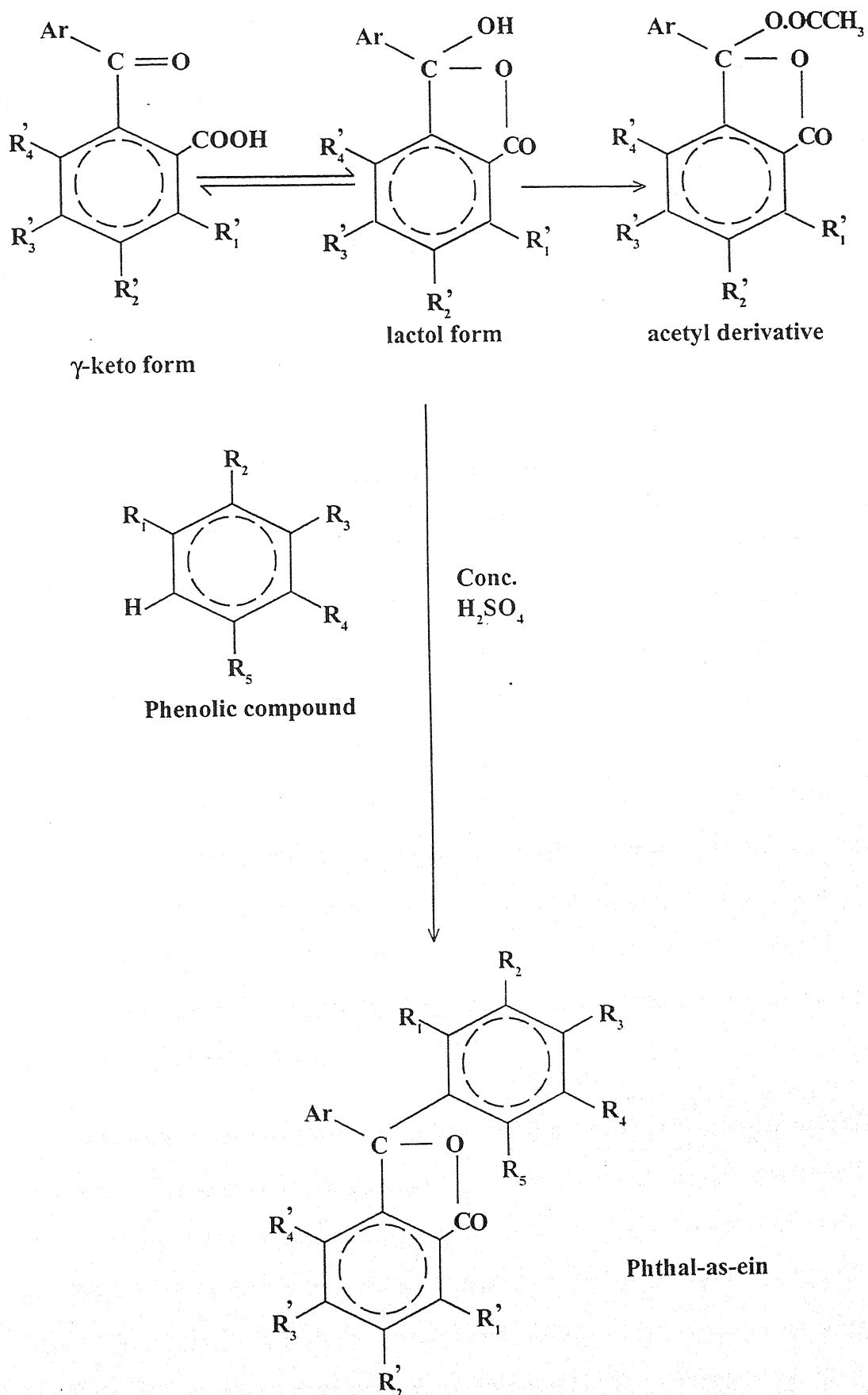


Figure 2.25

– OH (3100 – 3500 cm⁻¹)

IR spectra of acetyl derivatives of the acids were also investigated. It has been found that the peaks of > C = O in acetate (new peaks 1000 – 1250 cm⁻¹ and 1735 – 1760 cm⁻¹) and lactonic > C = O (1735 – 1790 cm⁻¹) were present. The peaks due to diarylkетonic > C = O (1675 – 1700 cm⁻¹), carboxylic > C = O (1695 – 1710 cm⁻¹), carboxylic –OH (2600-2700 cm⁻¹) and lactol – OH (3100 – 3500 cm⁻¹), which were originally present in acids were absent in the acetyl derivatives of the acids.

2.6 NMR SPECTROSCOPIC EXAMINATION OF γ -KETO ACIDS AND THEIR

ACETYL DERIVATIVES:

Chemical shifts recorded in the NMR spectra of the thirteen γ -keto acids and their derivatives further confirm the presence of the lactol tautomer in each case (τ = 4.2–4.35) which disappears in the case of the acetyl derivatives and a new chemical shift of O – COCH₃ (τ = 7.65 – 7.85) has been recorded. It makes it obvious that the γ -keto acids exist in keto as well as lactol form implying thereby that it is possible to condense these acids with different phenolic compounds giving unsymmetrical phthaleins. In addition the characteristic chemical shift referred to above, others mostly pertained to aromatic protons (τ = 1.85 – 3.45) depending on the chemical environment of the aromatic rings. However the chemical shift of –COOH in the keto form could not be recorded as the NMR spectroscopic examination was carried out and recorded on a Varian A – 60.

It now stands confirmed that the acids and their acetyl derivatives exhibit the phenomenon of ring chain tautomerism and most of the chemical reactions take place via the more stable lactol i. e. the ring form. It has now become quite certain that the cyclisation of γ -keto acids provides a hydroxyl group in the form of corresponding lactol. This lactol is capable of condensing with various hydroxy compounds resulting in the formation of novel analogues of phthaleins appropriately called phthal-as-eins. It also leaves no doubt for us to come to the conclusion that the acetylation of γ -

keto acids occurs through the ring tautomer i. e. the lactol form and also that the acetyl derivatives of the acids, phthal-as-eins also have cyclic structures.

The formation of the acetyl derivatives, phthal-as-eins, may be depicted in a manner shown on the following pages.

Gupta, Beg and coworkers²⁹⁻⁴⁸ have recently reported the preparation of a large number of mixed phthal-as-eins from γ -keto acids. These investigators have also shown that the lactol form of the γ -keto acids is actually involved in the synthesis of these compounds.

2.7 CHEMICAL STRUCTURE OF PHTHAL-AS-EINS:

In this section, the investigator has made an attempt to assign suitable and satisfactory chemical structure to the various synthesised novel analogues of phthaleins or more aptly the phthal-as-eins. The basis of assignment of the structures is the study of IR and NMR spectra of γ -keto acids used for synthesis of phthal-as-eins. The following representative dyes have been selected to establish the chemical structure:

A.1.3. 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein

B.1.3. 2-hydroxy-5-methylphenyl resorcinol tetrachloro phthal-as-ein

C.1.3. 2-hydroxy-5-methylphenyl resorcinol nitro phthal-as-ein

A.2.3. 5-chloro-2-methylphenyl resorcinol phthal-as-ein

B.2.3. 5-chloro-2-methylphenyl resorcinol tetrachloro phthal-as-ein

C.2.3 5-chloro-2-methylphenyl resorcinol nitro phthal-as-ein

A.3.3. (3-chloro-4-chloromethylphenyl) resorcinol phthal-as-ein

B.3.3 (3-chloro-4-chloromethylphenyl) resorcinol tetrachloro phthal-as-ein

C.3.3. (3-chloro-4-chloromethylphenyl resorcinol nitro phthal-as-ein

D.1.3. α -naphthyl resorcinol nitro phthal-as-ein

D.2.3. 2- anthracenyl resorcinol nitro phthal-as-ein

D.3.3. 3-phenanthryl resorcinol nitro phthal-as-ein

D.4.3. 3- acenaphthyl resorcinol nitro phthal-as-ein

For each of the above dyes a suitable molecular structure has been suggested on the basis of elemental analysis, molecular weight determination, identification and determination of characteristic functional groups. The study of the brominated product and determination of Br atoms in each case has been utilised to find out the number of resorcinol molecules in a dye. Each dye has also been subjected to caustic potash treatment that helped which helped us to assign the structures on a more confidently and precisely.

The IR spectra of the dyes and also that of their acetyl derivatives further support the structure of the dyes described in the following lines. Each dye shows peak due to lactonic $> C = O$ ($1735 - 1790 \text{ cm}^{-1}$) and the phenolic hydroxy group ($3300 - 3500 \text{ cm}^{-1}$). The peak due to the hydroxyl group does not occur in the IR spectra of the acetyl derivatives. On the other hand new ester peaks have been observed in the range of $1000 - 1250 \text{ cm}^{-1}$ and $1735 - 1760 \text{ cm}^{-1}$ in the spectra of these acetyl derivatives.

2.7.01 STRUCTURE OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL

PHTHAL-AS-EIN:

It was found convenient to prepare the dye by the condensation of 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid and resorcinol in presence of few drops of concentrated sulphuric acid as the condensing agent as described later in another chapter. The dye 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein with the molecular formula $C_{21}H_{16}O_5$, molecular weight 348 on acetylation lead to the formation of triacetyl

derivative. It indicated the presence of three phenolic -OH groups. The bromination of the dye with a predetermined amount of bromine, the dye yielded a tribromo derivative confirming the presence of a molecule of resorcinol in the dye molecule. The caustic potash treatment of the dye resulted in the formation of 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid and a molecule of resorcinol corresponding to each molecule of the dye. With an excess of bromine, the molecule yielded a molecule of the same acid and a molecule of tribromo resorcinol. Thus, on the basis of chemical evidences as described above the structure figure 2.26a has been assigned to the dye molecule.

2.7.02 STRUCTURE OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

The preparation of the dye 2-hydroxy-5-methylphenyl resorcinol tetrachloro phthal-as-ein was synthesised by the condensation of resorcinol and 2-(2'-hydroxy-5'-methylbenzoyl) tetrachloro benzoic acid in presence of concentrated sulfuric acid as the condensing agent as described in a subsequent chapter dealing with the experimental part of the work under study. The dye, as prepared, had the molecular formula $C_{21}H_{12}Cl_4O_5$ and a molecular weight of 486 in agreement with the former. The dye, on acetylation, yielded a triacetyl derivative and on bromination too with calculated amount of bromine formed a tribromo derivative. It conclusively indicated the presence of three phenolic hydroxy groups in the dye molecule. Thus, only one molecule of resorcinol is present in the dye molecule. Caustic potash treatment of the dye forms a molecule of 2-(2'-hydroxy-5'-methylbenzoyl) tetrachloro benzoic acid along with a molecule of resorcinol. If we assign the structure figure 2.26b to the dye molecules, all the above reactions can be easily explained. On treatment with an excess of bromine, the dye molecule gave the same acid with a molecule of tribromoresorcinol. All these reactions may be explained by assigning the structure 2.26b to the dye molecule.

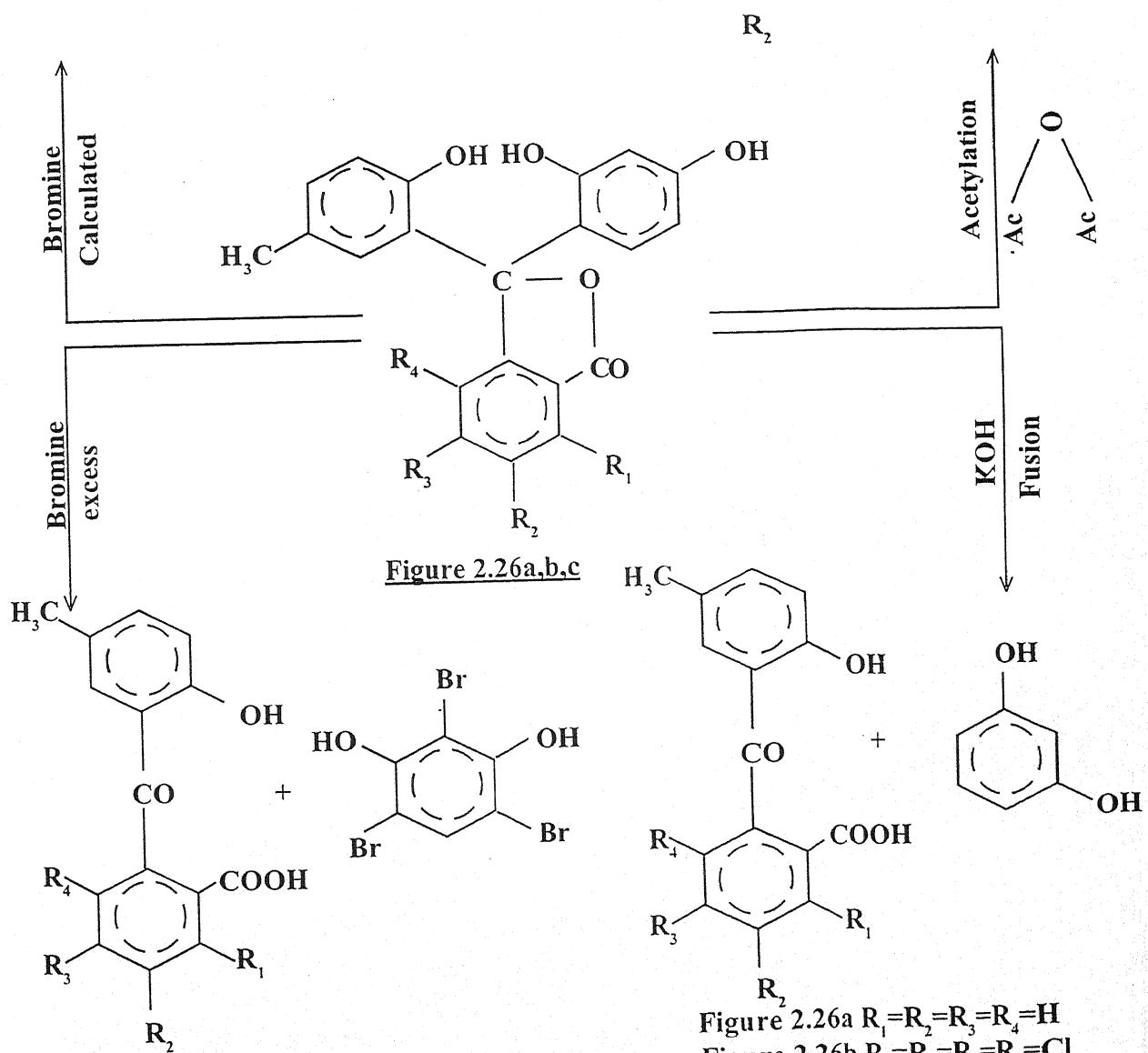
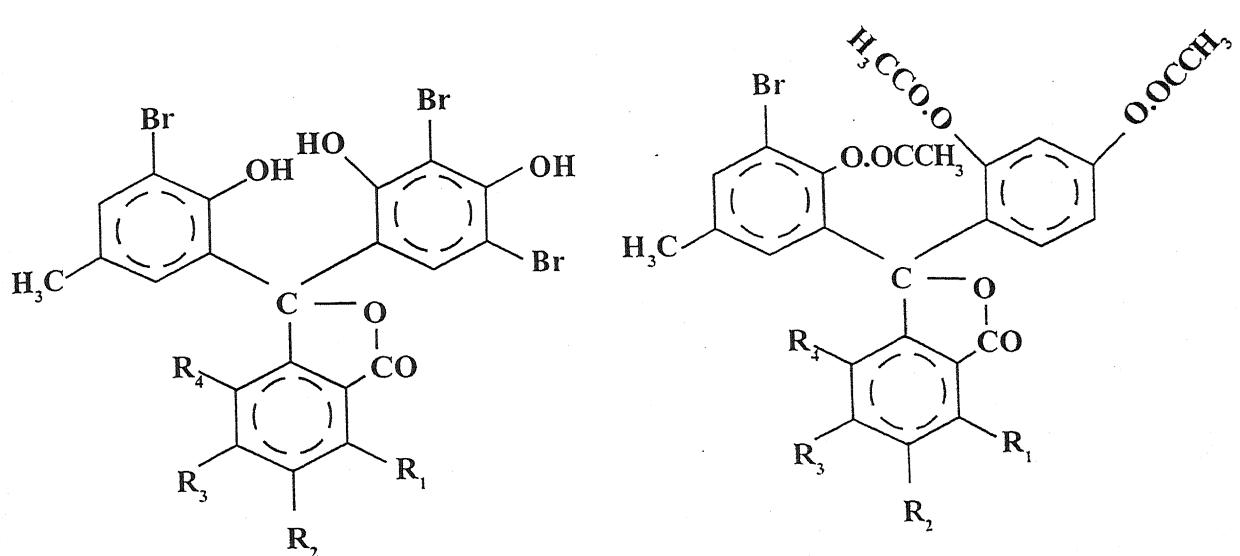


CHART A

2.7.03 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

Condensation of 2-(2'-hydroxy-5'-methylbenzoyl)-3-nitrobenzoic acid with resorcinol in the presence of the usual condensing agent sulphuric acid as described in a later chapter lead to the formation of this dye. The dye had the molecular formula $C_{21}H_{15}NO_7$ and a molecular weight of 393. On acetylation, the dye formed a triacetyl derivative and on bromination with calculated amount of bromine formed a tribromo derivative to indicate the presence of three phenolic -OH groups in the dye molecule. The dye was treated with caustic potash to yield a molecule of resorcinol and 2-(2'-hydroxy-5'-methylbenzoyl)-3-nitrobenzoic acid. Treatment with an excess of bromine also formed the same acid and tribromo resorcinol. The assignment of the structure LXIXc to the dye 2-hydroxy-5-methylphenyl resorcinol nitro phthal-as-ein justified the above reactions of the dye.

All the reactions of the dyes (figure 2.26 a, b and c) have systematically depicted in chart A

2.7.04 STRUCTURE OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

PHTHAL-AS-EIN:

The 5-chloro-2-methylphenyl resorcinol phthal-as-ein with a molecular formula of $C_{21}H_{15}ClO_4$ and molecular weight of 366 was prepared by the condensation of 2-(5'-chloro-2'-methylbenzoyl) benzoic acid with resorcinol in presence of a few drops of concentrated sulfuric acid as the condensing agent as described in detail in a subsequent chapter giving experimental details. On acetylation with acetic anhydride in presence of glacial acetic acid, the dye formed a diacetyl derivative and upon bromination with calculated amount of bromine formed a dibromo derivative to indicate the presence of one resorcinol molecule in the dye structure. The dye formed a molecule of 2-(5'-chloro-2'-methylbenzoyl) benzoic acid and a molecule of resorcinol on caustic potash treatment. The dye with excess of bromine yielded a molecule of the same acid and a molecule of tribromo resorcinol. The structure of molecule of the dye was assigned as in figure 2.27a on the basis of the above analytical evidence.

2.7.05 STRUCTURE OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

The dye 5-chloro-2-methylphenyl resorcinol tetrachloro phthal-as-ein was, as usual, prepared by the condensation of 2-(5'-chloro-2'-methylbenzoyl) tetrachloro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as per detailed procedure described in a later chapter. The molecular weight of the dye was found to be 504.5 and the molecular formula was $C_{21}H_{11}Cl_5O_4$. The dye was able to form the diacetyl and the dibromo derivative on acetylation and bromination with a calculated amount of bromine respectively. It showed the presence of only one molecule of resorcinol in the dye structure. Fusion of the dye with caustic potash formed 2-(5'-chloro-2'-methylbenzoyl) tetrachloro benzoic acid and a molecule of resorcinol. On treatment with an excess of bromine, the molecule formed the same acid and a molecule of tribromo resorcinol. All the chemi-

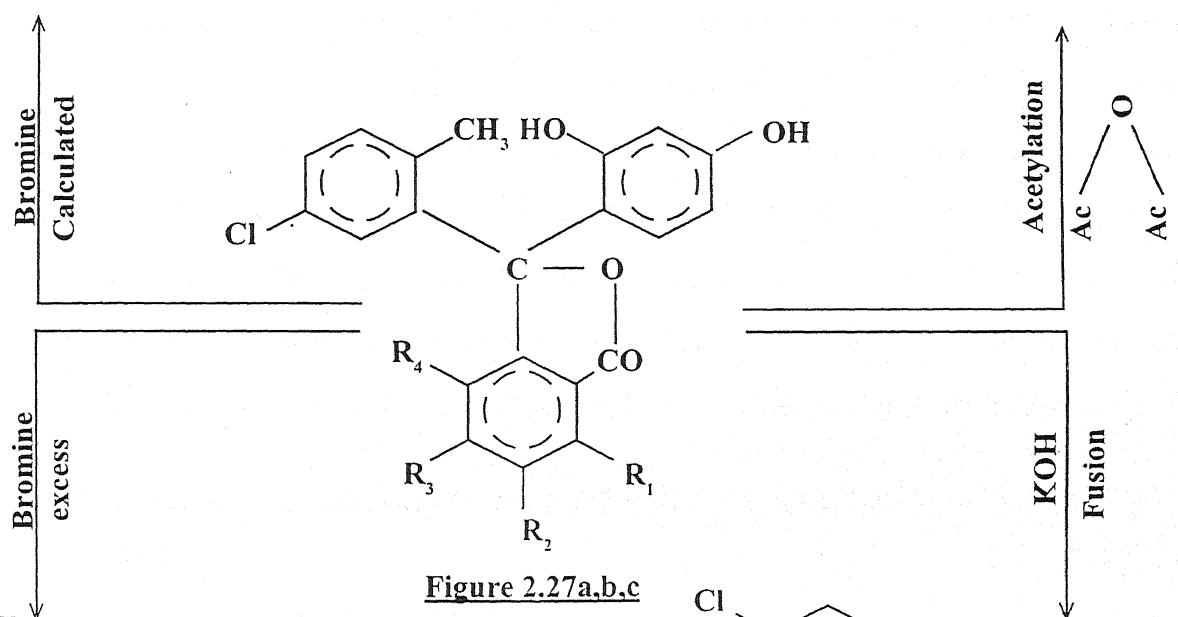
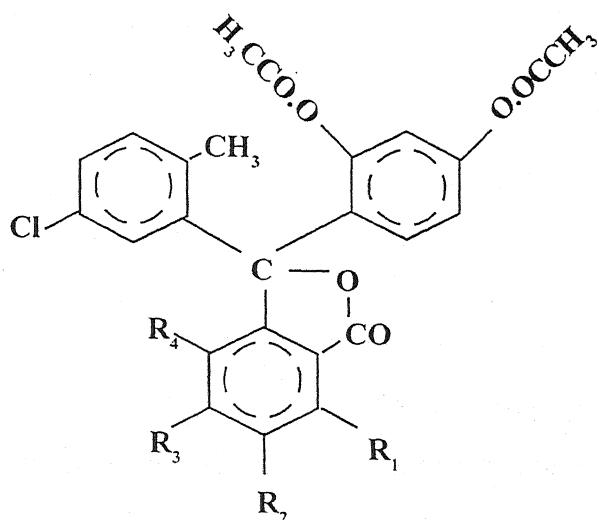
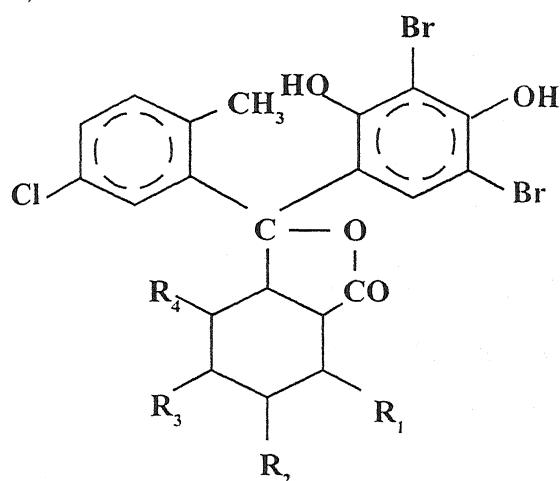


Figure 2.27a,b,c

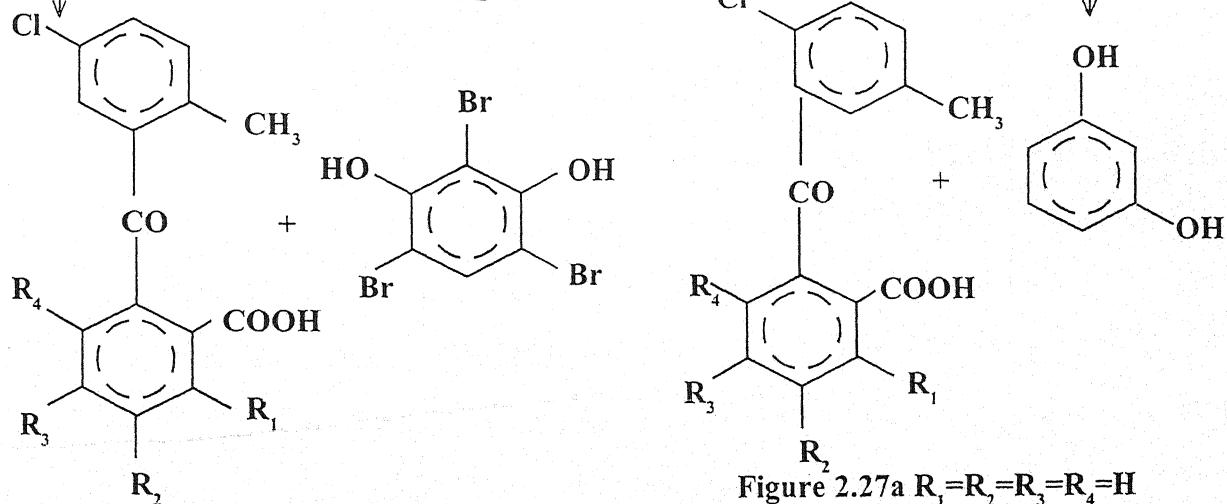


Figure 2.27a $R_1=R_2=R_3=R_4=H$

Figure 2.27b $R_1=R_2=R_3=R_4=Cl$

Figure 2.27c $R_1=R_2=R_3=H, R_4=NO_2$

CHART B

cal evidence described above lead one to assign the structure of this new dye as in figure 2.27b.

2.7.06 STRUCTURE OF 5-CHLORO-2-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

The dye 5-chloro-2-methylphenyl resorcinol nitro phthal-as-ein could be prepared by condensing 2-(5'-chloro-2'-methylbenzoyl) -3- nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent as per experimental details in a subsequent chapter. The dye was found to possess the molecular formula $C_{21}H_{14}ClO_6$ and a molecular weight of 411.5. It gave diacetyl derivative and dibromo derivative on acetylation and bromination with the requisite amount of bromine respectively. It indicated the presence of only one molecule of resorcinol in the dye molecule. The 2-(5'-chloro-2'-methylbenzoyl) -3 - nitro benzoic acid and a molecule of resorcinol were formed on fusion of the dye with caustic potash. Bromination of the dye with an excess of bromine formed a molecule of the same acid and tribromo resorcinol. The evidence as described above clearly substantiated the structure of the dye as depicted in structure (figure 2.27c).

All the reactions of the dyes 2.27a, 2.27b and 2.27c have been graphically displayed in chart B

2.7.07 STRUCTURE OF (3-CHLORO-4-CHLOROMETHYLPHENYL) RESORCINOL PHTHAL-AS-EIN:

The dye (3-chloro-4-chloromethylphenyl) resorcinol phthal-as-ein has been prepared by the condensation of 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid with resorcinol with four or five drops of concentrated sulphuric acid as the condensing agent as detailed later in a subsequent chapter on experimental procedures. The dye molecule was found to have the formula $C_{21}H_{14}Cl_2O_4$ and a molecular weight of 401. It formed a diacetyl derivative and a dibromo derivative on acetylation and treatment with calculated amount of bromine respectively indicating the presence of only one molecule of resorcinol in the dye molecular structure. The dye, on fusion with caustic potash, formed a molecule of resorcinol and 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid. Treatment with an excess of bromine lead to the formation of 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid once again and a molecule of dibromo resorcinol. Hence the structure of the dye could be formulated as depicted in figure 2.28a.

2.7.08 STRUCTURE OF (3-CHLORO-4-CHLOROMETHYLPHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

The condensation of 2-(3'-chloro-4'-chloromethylbenzoyl) terachloro benzoic acid with resorcinol in presence of some drops of concentrated sulphuric acid as a condensing agent as per details given in a later chapter was all that was required to synthesize (3-chloro-4-chloromethylphenyl) resorcinol tetrachloro phthal-as-ein which had a molecular formula of $C_{21}H_{10}Cl_6O_4$ and a molecular weight of 539. On acetylation the dye formed a diacetyl derivative while on bromination with a calculated amount of bromine yielded a dibromo derivative. On caustic potash fusion of the dye, 2-(3'-chloro-4'-chloromethylbenzoyl) tetrachloro benzoic acid and a molecule of resorcinol was formed. On treatment with an excess of bromine, the dye formed 2-(3'-chloro-4'-chloromethylbenzoyl) tetrachloro benzoic acid and dibromo resorcinol. These results lead us to conclude that the structure of the dye was as depicted in figure 2.28b.

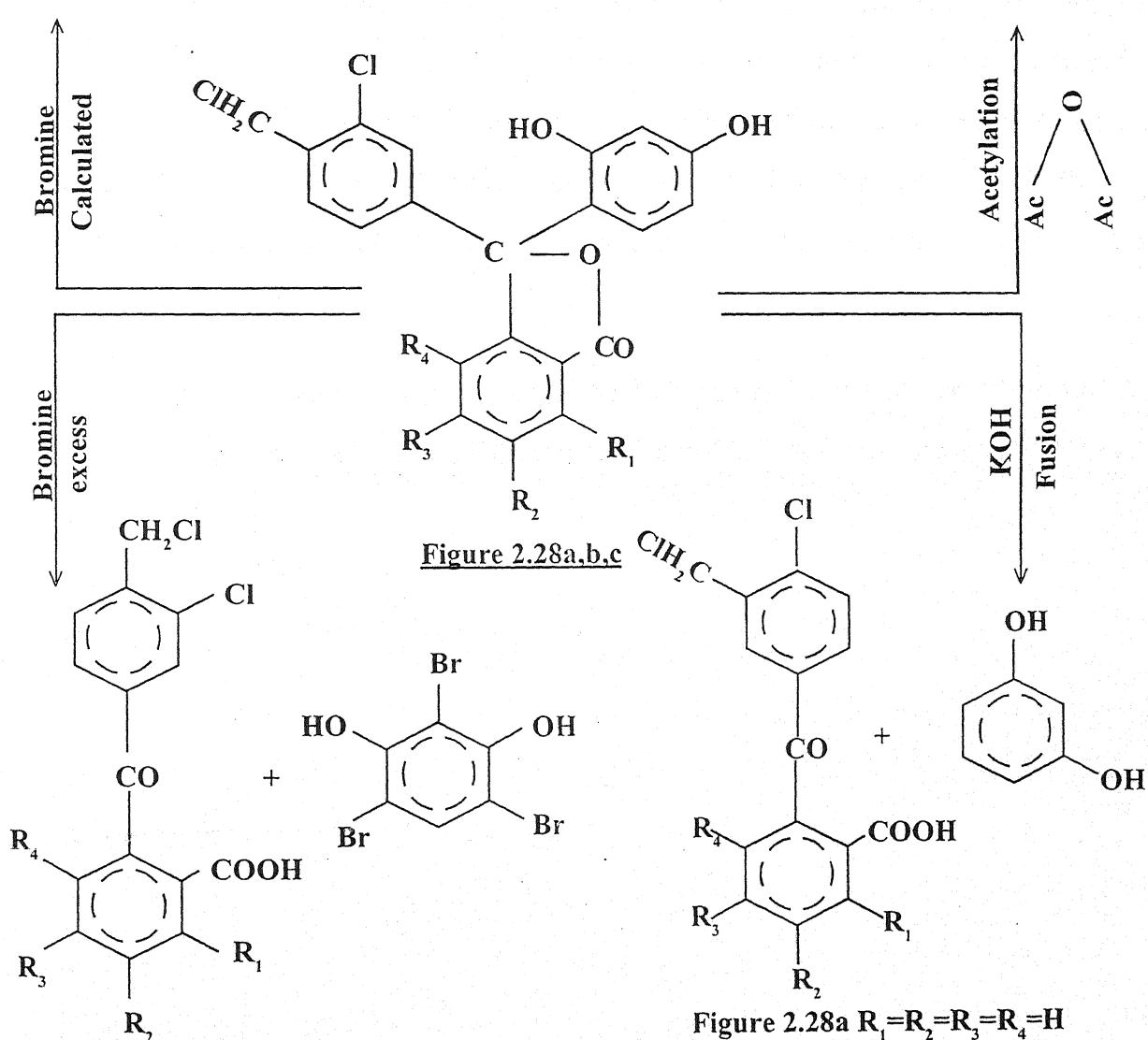
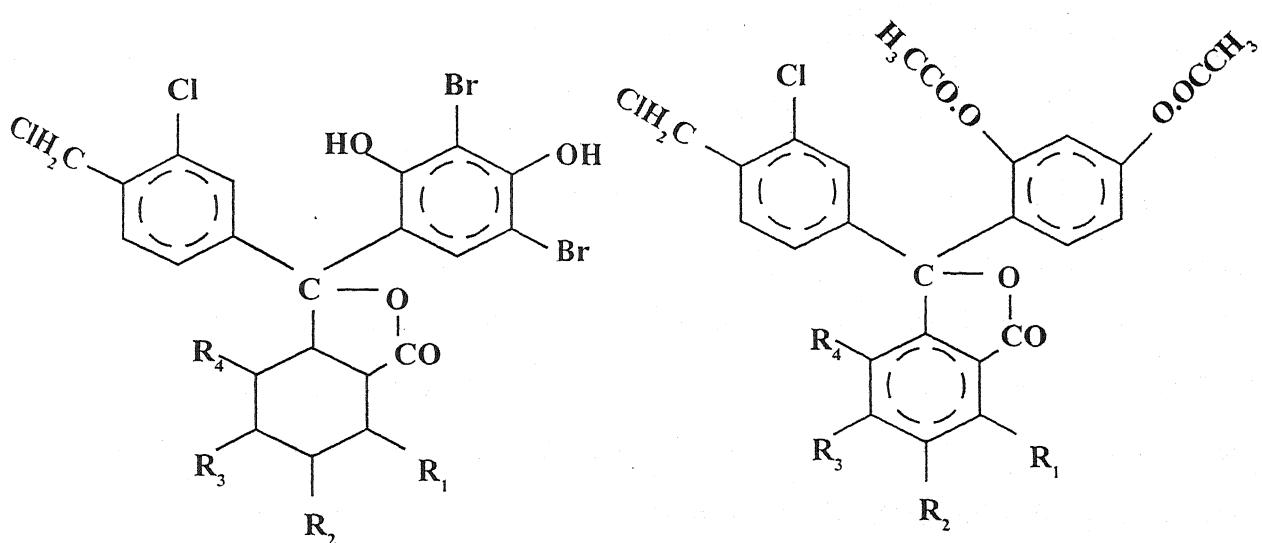


Figure 2.28a $R_1=R_2=R_3=R_4=H$

Figure 2.28b $R_1=R_2=R_3=R_4=Cl$

Figure 2.28c $R_1=R_2=R_3=H, R_4=NO_2$

CHART C

2.7.09 STRUCTURE OF (3-CHLORO-4-CHLOROMETHYLPHENYL RESORCINOL NITRO PHTHAL-AS-EIN:

The dye (3-chloro-4-chloromethylphenyl resorcinol nitro phthal-as-ein with the molecular weight of 446 and molecular formula of $C_{21}H_{13}NCl_2O_6$ could be conveniently prepared by the condensation of resorcinol with 2-(3'-chloro-4'chloromethylbenzoyl)-3-nitro benzoic acid in presence of a few drops of concentrated sulphuric acid as a condensing agent following details given in the chapter on the experimental part. The dye formed a diacetyl derivative on acetylation and a dibromo derivative on treatment with calculated amount of bromine. This indicates that a molecule of resorcinol is present in the molecular structure of dye. 2-(3'-chloro-4'chloromethylbenzoyl)-3-nitro benzoic acid and a molecule of resorcinol were formed on caustic potash fusion of the dye. Treatment of the dye with an excess of bromine formed tribromo resorcinol and 2-(3'-chloro-4'chloromethylbenzoyl)-3-nitro benzoic acid. On the basis of the evidence cited in the above lines, the dye was assigned the structure depicted in figure 2.28c.

The chemical reactions involved in the establishment of the structure of the dye depicted in figures 2.28a figure 2.28b and in figure 2.28c are graphically presented in chart C.

2.7.10 STRUCTURE OF α -NAPHTHYL RESORCINOL NITRO PHTHAL-AS-

EIN:

The dye α -naphthyl resorcinol nitro phthal-as-ein was conveniently prepared by the condensation of 2-(α -naphthoyl)-3-nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent. It was found that the dye had a molecular formula $C_{24}H_{15}NO_6$ and a molecular weight of 413. The dye formed a diacetyl derivative on acetylation and dibromo derivative on bromination with a calculated amount of bromine. Thus, only one molecule of resorcinol could be present in the molecular structure of the dye. 2-(α -naphthoyl)-3-nitro benzoic acid and a molecule of resorcinol was formed on the caustic potash treatment of the dye. However, on treatment with an excess of bromine, the dye formed 2-(α -naphthoyl)-3-nitro benzoic acid along with a molecule of tribromo resorcinol. The evidence so deduced was clear enough for us to assign the structure depicted in figure 2.29a to the dye.

2.7.11 STRUCTURE OF (2- ANTHRACENYL) RESORCINOL NITRO PHTHAL-AS-EIN:

The dye (2- anthracenyl) resorcinol nitro phthal-as-ein was found to possess a molecular formula of $C_{28}H_{17}NO_6$ and a molecular weight of 463. It was prepared by condensing 2-(2'-anthracenoyl)-nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid present as the condensing agent. The dye was able to form the diacetyl derivative upon acetylation and a dibromo derivative on bromination with a measured amount of bromine. Obviously one molecule of resorcinol was present in the dye molecule's structure. The dye was subjected to caustic potash treatment when it yielded 2-(2'-anthracenoyl)- nitro benzoic acid along with a molecule of resorcinol. The treatment of the dye with excess of bromine yielded 2-(2'-anthracenoyl)- nitro benzoic acid again and a molecule of tribromo resorcinol. The dye could be conveniently assigned the structure depicted in figure 2.29b on the basis of above observations.

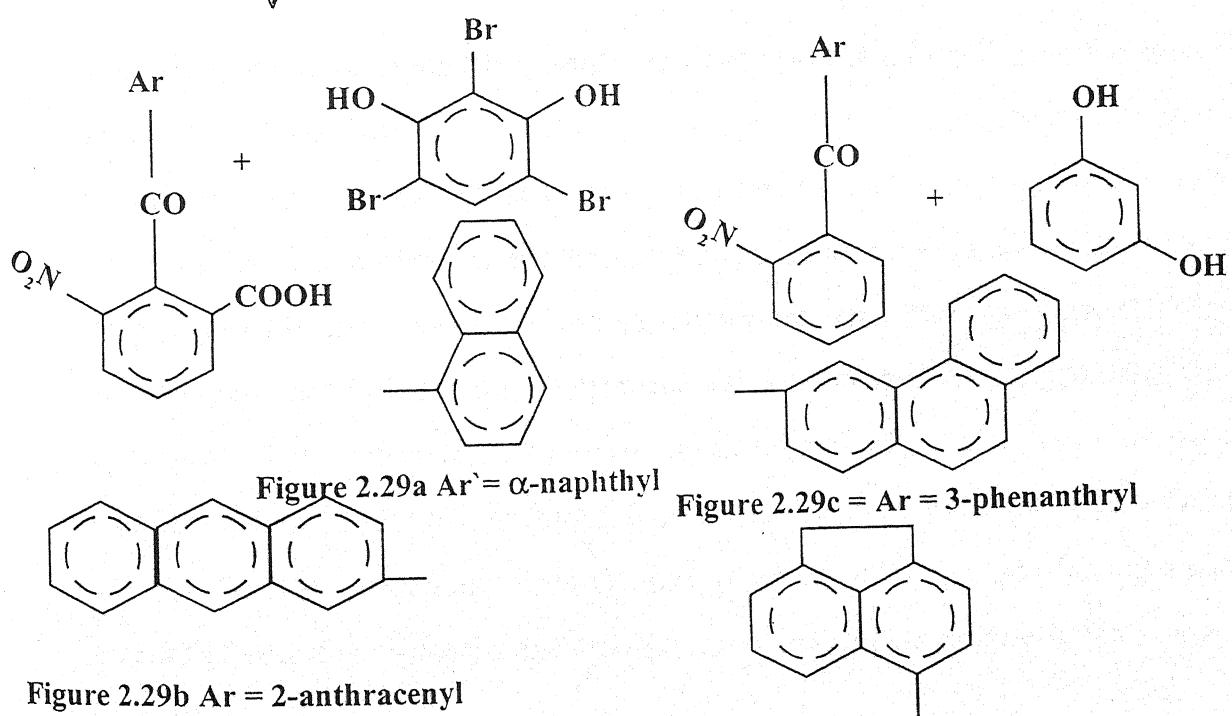
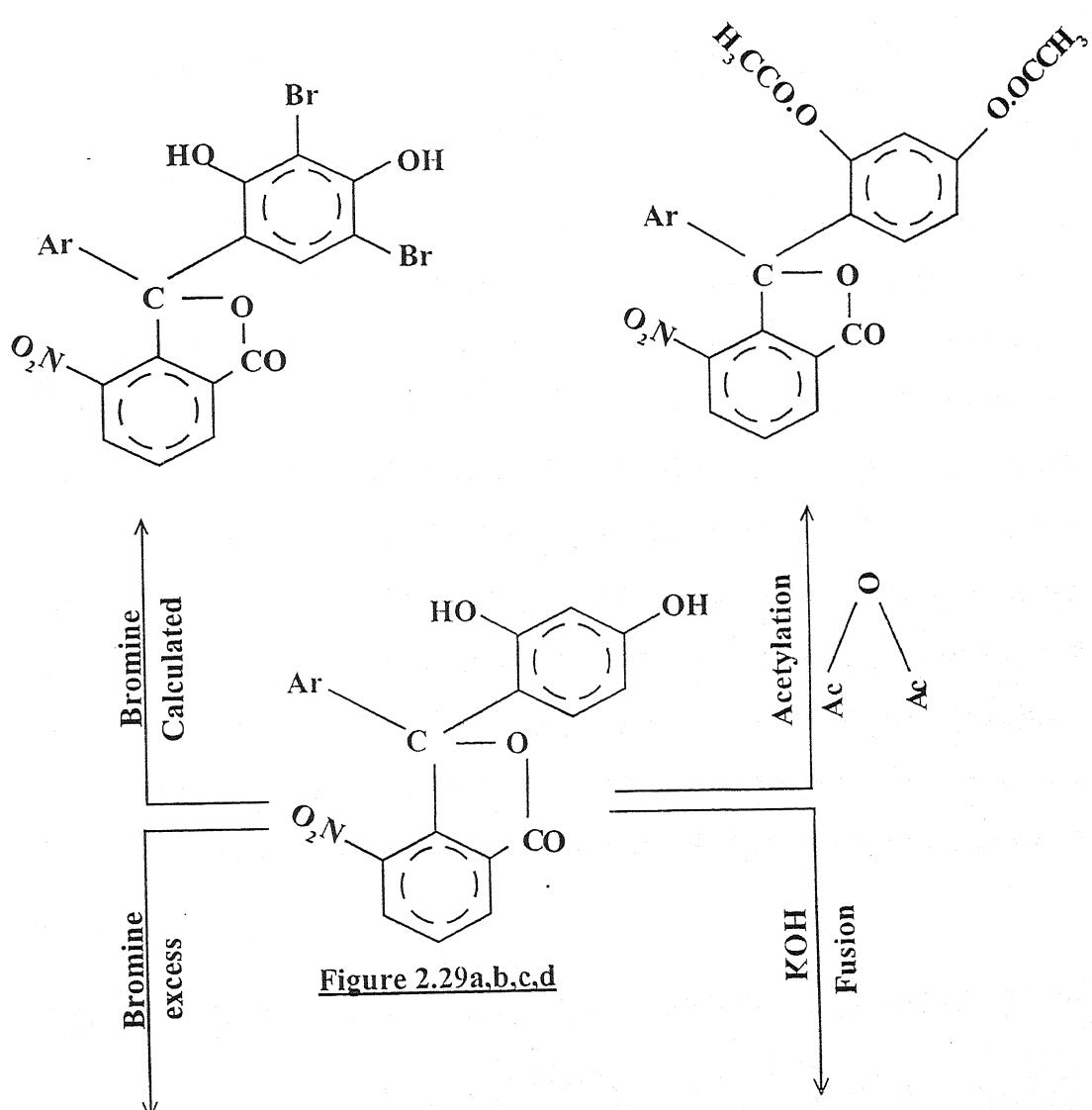


CHART D Figure 2.29d = Ar = 3-acenaphthyl

2.7.12 STRUCTURE OF (3-PHENANTHRYL) RESORCINOL NITRO PHTHAL-

AS-EIN:

The dye 3-phenanthryl resorcinol nitro phthal-as-ein was prepared by the condensation of 2-(3'-phenanthroyl)-3-nitro benzoic acid with resorcinol in presence of a few drops of concentrated sulphuric acid as the condensing agent. It was found that the dye had a molecular formula $C_{28}H_{17}NO_6$ and a molecular weight of 463. The dye formed a diacetyl derivative on acetylation and a dibromo derivative on treatment with calculated amount of bromine. This indicates that a molecule of resorcinol is present in the molecular structure of dye. 2-(3'-phenanthroyl)-3-nitro benzoic acid and a molecule of resorcinol were formed on caustic potash treatment of the dye. Further the treatment of the dye with excess of bromine also gave 2-(3'-phenanthroyl)-3-nitro benzoic acid in addition to a molecule of tribromo resorcinol. Thus, one could safely assign the structure depicted in figure 2.29c to the dye on the basis of reactions cited above.

1.7.13 STRUCTURE OF 3- (ACENAPHTHYL) RESORCINOL NITRO PHTHAL-

AS-EIN:

The novel dye 3- (acenaphthyl) resorcinol nitro phthal-as-ein having the molecular weight of 439 and molecular formula of $C_{26}H_{17}NO_6$ could be conveniently prepared by the condensation of resorcinol with 2-(3'-acenaphthoyl)-3-nitro benzoic acid in presence of a few drops of concentrated sulphuric acid as a condensing agent following details given in the chapter on the experimental part. The dye formed a diacetyl derivative on acetylation and a dibromo derivative on treatment with calculated amount of bromine. This indicates that a molecule of resorcinol is present in the molecular structure of dye. 2-(3'-acenaphthoyl)-3-nitro benzoic acid and a molecule of resorcinol were formed on caustic potash fusion of the dye. Treatment of the dye with an excess of bromine formed tribromo resorcinol and 2-(3'-acenaphthoyl)-3-nitro ben-

zoic acid. On the basis of the evidence cited in the above lines, the dye was assigned the structure depicted in figure 2.28d.

All the chemical reactions involved in the assignment of structures depicted in figure 2.28a,b, c and d have been graphically depicted in chart D.

Table 2.01

IR SPECTRA OF γ -KETOACIDS AND THEIR ACETYL DERIVATIVES

Acids and their acetyl derivatives	Diaryl ketonic $>C=O$	Carboxyl $>C=O$	Lactonic $>C=O$	Carboxyl -OH	Lactol -OH	Ester group
2.7.01 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid	1685	1710	1735	2660 (weak)	3460	1750,1235,1230 and 1010
Acetyl derivative			1790			
2.7.02 2-(5'-chloro-2'-methylbenzoyl) benzoic acid	1690	1705	1745	2640(weak)	3440	
Acetyl derivative						1760,1240,1210 and 1035
2.7.03 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid	1695	1710	1740	2645 (weak)	3470	
Acetyl derivative			1782			1755,1250, 1220 and 1010
2.7.04 2-(2'-hydroxy-5'-methylbenzoyl) tetrachloro benzoic acid	1690	1705	1740	2665 (weak)	3150	
Acetyl derivative						1780,1250,1230 and 1010
2.7.05 2-(5'-chloro-2'methylbenzoyl) tetrachloro benzoic acid	1685	1700	1740	2670(weak)	3500	
Acetyl derivative			1785			1755,1250,1220 and 1010
2.7.06 2-(3'-chloro-4'-chloromethylbenzoyl) tetrachlorobenzoic acid	1675	1695	1735	2630(weak)	3290	
Acetyl derivative						1745,1250,1220 and 1030
2.7.07 2-(2'-hydroxy-5'methylbenzoyl) -3-nitrobenzoic acid	1682	1695	1740	2650	3300	
Acetyl derivative						1750,1250,1220 and 1030
2.7.08 2-(5'-chloro-2'-methylbenzoyl) -3-nitro benzoic acid	1680	1690	1740	2610	3450	
Acetyl derivative						1740,1240,1210 and 1010
				1780		

Ester group

Acids and their acetyl derivatives

2.7.09 2-(3'-chloro-4'-chloromethylbenzoyl)-3-nitro-benzoic acid

Acetyl derivative

2.7.10 2-(α -naphthoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.11 2-(2'-anthracenoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.12 2-(3'-phenanthroyl)-3-nitro benzoic acid

Acetyl derivative

2.7.13 2-(3'-acenaphthoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.14 2-(3'-benzoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.15 2-(3'-benzyl)-3-nitro benzoic acid

Acetyl derivative

2.7.16 2-(3'-cinnamoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.17 2-(3'-acetylbenzoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.18 2-(3'-acetyl-4'-nitrobenzoyl)-3-nitro benzoic acid

Acetyl derivative

2.7.19 2-(3'-acetyl-4'-nitrobenzyl)-3-nitro benzoic acid

Acetyl derivative

2.7.20 2-(3'-acetyl-4'-nitrobenzylidene)-3-nitro benzoic acid

Acetyl derivative

2.7.21 2-(3'-acetyl-4'-nitrobenzylidene)-3-nitro-2,4-dihydro-5H-1,3-dioxole-5-carboxylic acid

Acetyl derivative

2.7.22 2-(3'-acetyl-4'-nitrobenzylidene)-3-nitro-2,4-dihydro-5H-1,3-dioxole-5-carboxylic acid

Acetyl derivative

2.7.23 2-(3'-acetyl-4'-nitrobenzylidene)-3-nitro-2,4-dihydro-5H-1,3-dioxole-5-carboxylic acid

Acetyl derivative

2.7.24 2-(3'-acetyl-4'-nitrobenzylidene)-3-nitro-2,4-dihydro-5H-1,3-dioxole-5-carboxylic acid

Acetyl derivative

Carboxyl >C=O

Lactol -OH

Ester group

Table 2.02

NMR SPECTRA OF γ -KETOACIDS AND THEIR ACETYL DERIVATIVES

<u>Acids and their acetyl derivatives</u>	<u>Solvent</u>	<u>Chemical shift (τ)</u>
2-(2-hydroxy-5-methylbenzoyl) benzoic acid	$CDCl_3$	1.95-2.05(m,4 ring protons); 2.25-2.85(m, 3 substituted ring protons); 7.5s (singlet ring methyl protons); 4.45 (singlet, phenolic -OH proton);4.35 (singlet, lactol -OH proton).
Acetyl derivative	$CDCl_3$	1.95-2.05(m,4 ring protons); 2.25-2.85(m, 3 substituted ring protons); 7.55 (singlet ring methyl protons); 4.45 (singlet, phenolic -OH proton); 7.65 (singlet, 3 -OOC.CH ₃ protons).
2-(5'-chloro-2'-methylbenzoyl) benzoic acid	$CDCl_3$	2.30-2.95(m,4 ring protons); 2.20-2.80(m, 3 substituted ring protons); 7.50 (singlet, three methyl protons);4.25 (singlet, lactol -OH proton).
Acetyl derivative	$CDCl_3$	2.30-2.95 (m,4 ring protons); 2.20-2.80(m, 3 substituted ring protons); 7.50 (singlet ring methyl protons); 7.65 (singlet, 3 -OOC.CH ₃ protons)..
2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid	DMSO	2.05-2.20,(m,4 ring protons); 2.25-2.90,(m, 3 substituted ring protons);4.35 (br singlet, lactol -OH proton); 6.5, (s, 2 -CH ₂ Cl protons...
Acetyl derivative	DMSO	2.05-2.95,(m,7 unsymmetrical aromatic protons) 7.60 (s, 3 - OOC.CH ₃ protons; 6.45, (s, 2 -CH ₂ Cl protons..
2-(2-hydroxy-5'-methylbenzoyl)tetrachloro benzoic acid	$CDCl_3$	2.20-2.85,(m,3 ring protons); 7.55, (singlet, three methyl protons);4.45 (singlet, phenolic -OH proton);4.35 (singlet, lactol -OH proton).
Acetyl derivative	$CDCl_3$	2.20-2.85,(m,3 ring protons); 7.55, (singlet, three methyl protons);7.65, (singlet 6, two -OOC.CH ₃ protons);

Chemical shift (δ)

<u>Acids and their acetyl derivatives</u>	<u>Solvent</u>	<u>Chemical shift (δ)</u>
2-(5'-chloro-2'-methylbenzoyl) tetrachloro benzoic acid	CDCl_3	2.25-2.85,(m,3 ring protons); 7.55, (singlet, three methyl protons);4.20 (singlet, lactol -OH proton).
Acetyl derivative	CDCl_3	2.25-2.85,(m,3 ring protons); 7.52, (singlet, three methyl protons);7.65(singlet,3 -OOC. CH_3 protons).
2-(3'-chloro-4' chloromethylbenzoyl)	CDCl_3	2.18-2.95,(m,3 ring protons); 4.30 (br singlet, lactol -OH proton); 6.42, (s, 2 - CH_2Cl protons)
tetrachlorobenzoic acid		
Acetyl derivative	CDCl_3	2.15-2.90,(m,3 ring protons);7.60 (singlet, 3 -OOC. CH_3 protons); 6.45, (s, 2 - CH_2Cl protons.)
2-(2'-hydroxy-5'-methylbenzoyl -3-nitro benzoic acid	CDCl_3	1.90-2.05, (m, 3 nitro ring protons); 2.15-2.80 (m, 3 other ring protons); 7.55 (singlet, 3 - CH_3 protons); 4.30, (s, lactol -OH proton); 4.45, (s, phenolic -OH proton)
Acetyl derivative	CDCl_3	1.90-2.05, (m, 3 nitro ring protons); 2.15-2.80 (m, 3 other ring protons); 7.55 (singlet, 3 - CH_3 protons); 7.65, (S, 6 protons of two -OOC. CH_3)
2-(5'-chloro-2'-methylbenzoyl)-3-nitro benzoic acid	CDCl_3	1.95-2.10, (m, 3 nitro ring protons); 2.25-2.85 (m, 3 other ring protons); 7.55 (singlet, 3 - CH_3 protons); 7.65, (S,3 protons of proton).
Acetyl derivative	CDCl_3	1.95-2.10, (m, 3 nitro ring protons); 2.25-2.85 (m, 3 other ring protons); 7.55 (singlet, 3 - CH_3 protons); 7.65, (S,3 protons of -OOC. CH_3)
2-(3'-chloro-4'-chloromethylbenzoyl)-3-nitro-benzoic acid DMSO		2.22-3.40, (m, 6 unsymmetrical ring protons); 4.32 (br. S, lactol proton; 6.45 (s, 2 - CH_2Cl protons)
Acetyl derivative	DMSO	2.10-3.35, (m, 6 unsymmetrical ring protons); 7.62 (s, 3 -OOCCH3 protons; 6.42 , (s, 2 - CH_2Cl protons)

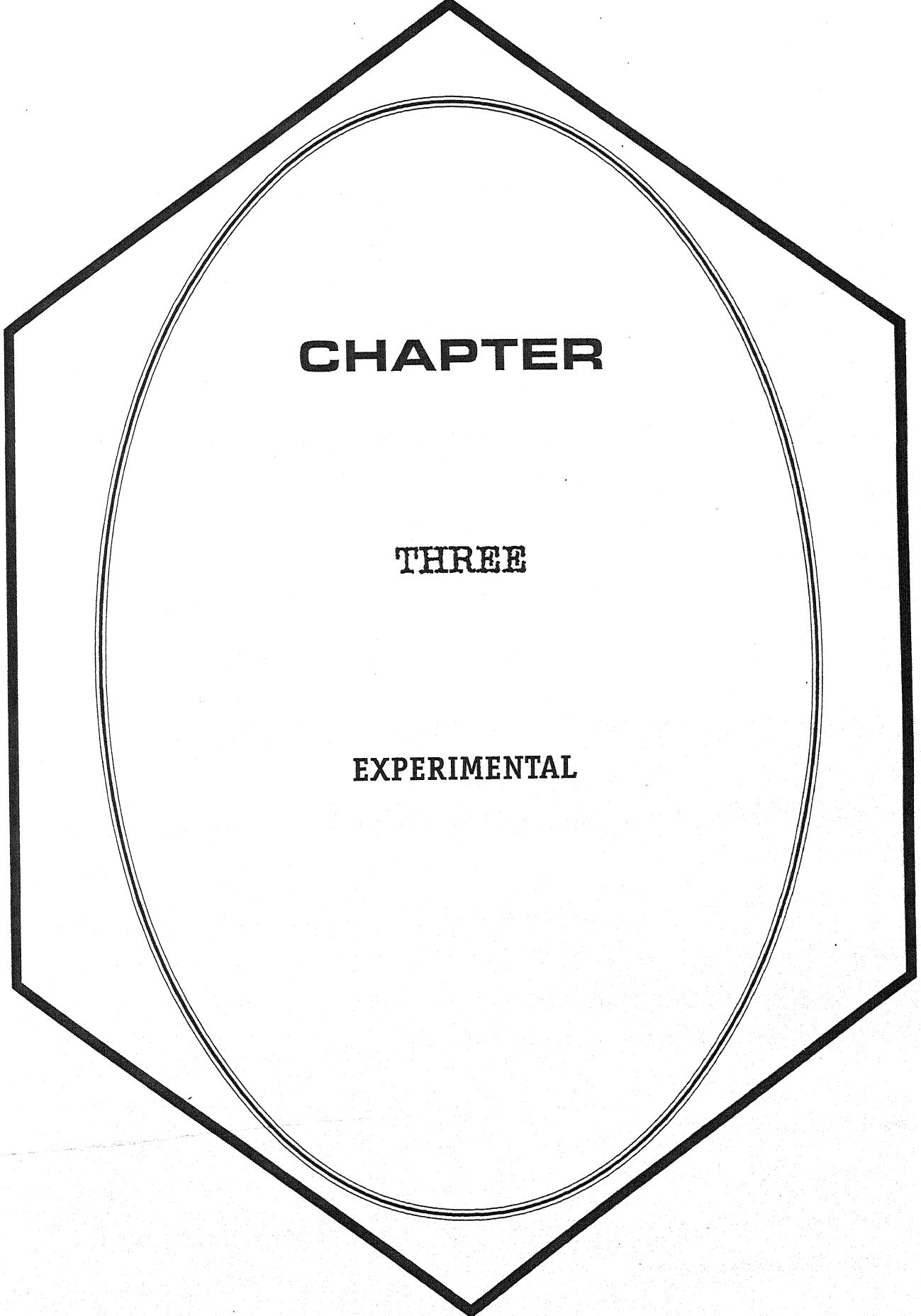
Acids and their acetyl derivatives**Chemical shift (τ)**

Solvent	Chemical shift (τ)
CDCl ₃	1.70-2.82 (m, 10 aromatic protons); 4.30, (br. S, Lactol -OH proton)
CDCl ₃	1.75-2.85 (m, 10 aromatic protons); 7.75, (. S, 3 -OOC.CH ₃ protons)
Acetyl derivative	
CDCl ₃	1.95-2.95, (m, 12 aromatic protons); 4.35, (br. S, Lactol -OH proton)
Acetyl derivative	
CDCl ₃	2.05-3.10 (m, 12 aromatic protons); 7.72, (S, 3 -OOC.CH ₃ protons)
CDCl ₃	2.15-3.25(m, 12 aromatic protons); 4.35, (br. S, 1 Lactol -OH proton)
Acetyl derivative	
CDCl ₃	2.05-3.10 (m, 12 aromatic protons); 7.65, (S, -OOC.CH ₃ protons)
2-(3'-phenanthroyl)-3-nitro benzoic acid	
CDCl ₃	2.15-3.25(m, 8 unsymmetrical ring protons); 4.30, (br. S, 1 Lactol -OH proton);7.40, (m, 4 (CH ₂) ₂ protons).
Acetyl derivative	
CDCl ₃	2.10-3.35 (m, 8 aromatic ring protons); 7.70, (S, 3 -OOC.CH ₃ protons); 7.45 (m, 4 (CH ₂) ₂ protons).
2-(3'-acenaphthoyl)-3-nitro benzoic acid	
Acetyl derivative	

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CHAPTER

THREE

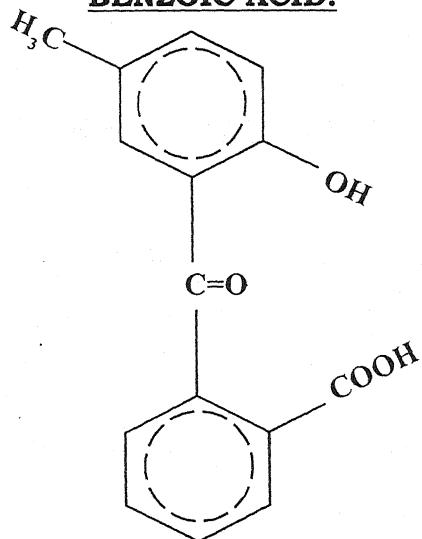
EXPERIMENTAL

EXPERIMENTAL

A.1

3.1 DYES DERIVED FROM 2-(2'HYDROXY-5'-METHYLBENZOYL)

BENZOIC ACID:



2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid

Figure 3.01

3.1A PREPARATION OF 2-(2'HYDROXY-5'-METHYLBENZOYL) BENZOIC

ACID:

The acid was prepared by carrying out Friedel Crafts reaction between p-cresol (dry AR, 85 ml) and phthalic anhydride (15.5 g, about 0.1 mole) while anhydrous AlCl_3 (27.0g, about 0.2 moles) was used as a catalyst. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 35°C by adding AlCl_3 in instalments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until evaporation of HCl ceased.

The heavy dark coloured complex was decomposed by the addition of 30ml concentrated hydrochloric acid in 250ml-ice cold water. The excess of p-cresol was removed by distillation. The residue was extracted three four times with boiling 10 % solution of sodium carbonate and filtered. The acid was precipitated from

the filtrate by the gradual addition of concentrated sulphuric acid. It was filtered off, washed well with cold water, dried and crystallised from acetone. It had a melting point of 182-183°C. It was found to be soluble in hot water, acetone and methanol. Yield 16.0 g.

Anal. For. : $C_{15}H_{12}O_4$ (mol. Wt. = 256)

Calc. : C, 70.31; H, 4.69;

Found : C, 70.22; H, 4.67.

3.1B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.2 g of the acid 3.5 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 120-130°C for about four hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of a light brown solid, m.p. 190°C. It is soluble in acetone, chloroform and acetic acid. Yield 0.98 g.

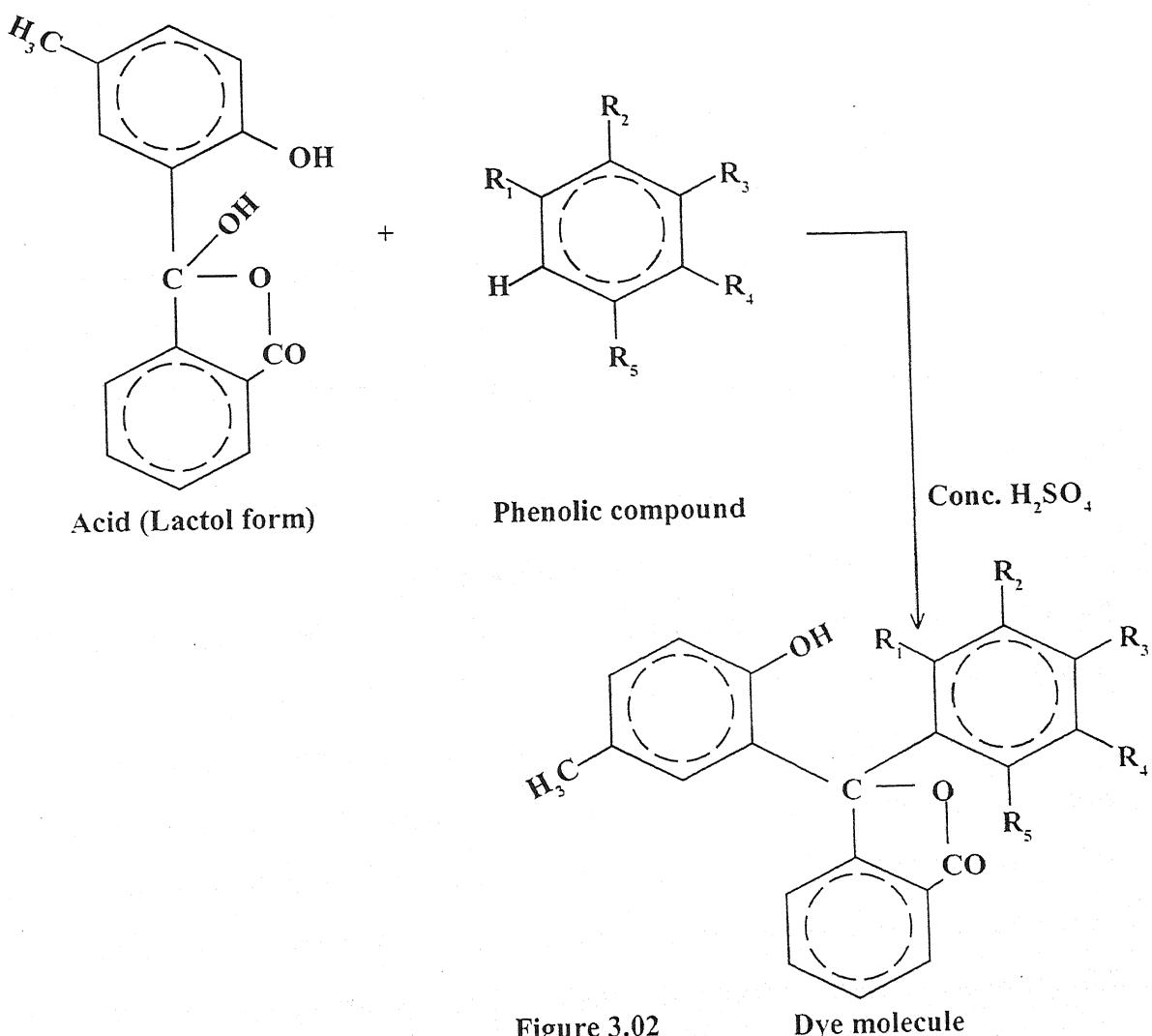
Anal. For. : $C_{19}H_{16}O_6$ or $C_{15}H_{10}O_4(OC.CH_3)_2$ (Mol. Wt. = 340)

Calc. : C, 67.06; H, 4.71; acetyl, 25.29

Found : C, 66.97; H, 4.69; acetyl, 25.21.

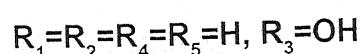
The dyes prepared from the acid may be represented by the following structures:

PLEASE TURN OVER

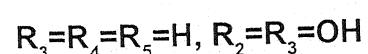


DYES:

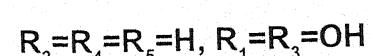
3.1.1 (2-hydroxy-5-methylphenyl) phenol phthal-as-ein:



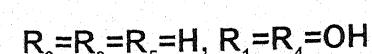
3.1.2 (2-hydroxy-5-methylphenyl) catechol phthal-as-ein:



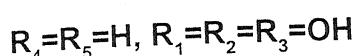
3.1.3 (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein:



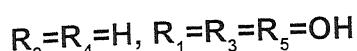
3.1.4 (2-hydroxy-5-methylphenyl) hydroquinone phthal-as-ein:



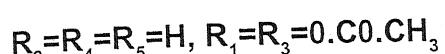
3.1.5 (2-hydroxy-5-methylphenyl) pyrogallol phthal-as-ein:



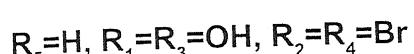
3.1.6 (2-hydroxy-5-methylphenyl) phloroglucinol phthal-as-ein:



3.1.7 (2-acetoxy-5-methylphenyl) diacetyl resorcinol phthal-as-ein:



3.1.8 (3-bromo-2-hydroxy-5-methylphenyl) dibromo resorcinol phthal-as-ein:



3.1.1 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) PHENOL

PHthal-as-ein:

A homogenized mixture of 1.5 g of the acid and 1.2 g of phenol was condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-170°C for about four and a half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The reddish pink solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum dessicator. Yield 1.3g.

The purity of the dye was tested by paper chromatography adopting technique

1A.1b.

Paper used	Whatman No 1
Mobile phase	Butanol saturated with ammonia
Developing agent	1% aqueous caustic soda
Reference dye	Phenolphthalein

A 25-cm X 10 cm strip of Whatman filter paper was cut and a very dilute solution was spotted with a micro syringe on a base line 3.0-cm from the bottom end. Similarly, a very dilute aqueous solution of the reference dye was also spotted 3.0 cm away from the first spot on the base line. The mobile phase was allowed to run

for thirteen hours. The paper was then taken out, dried and sprayed with the developing agent. The developed chromatogram revealed only one spot for each of the two dyes. This was enough to confirm the homogeneity and purity of the dye.

Found R _f (Phenolphalein):	0.93
5-methylphenyl) phenol phthal-as-ein:	0.92
Reported R _f (Phenolphthalein)	0.93

The pinkish red coloured microcrystalline dye has a m.p. 182-184°C. The ethanolic solution of the dye is light yellow in colour that turns into pink on adding a drop of an alkali. In strong basic medium, it gives intense pink colour.

Anal. For.: C₂₁H₁₆O₄ (Mol. Wt. 332)

Calc. : C, 75.9; H, 4.82

Found : C, 75.79; H, 4.78

3.1.2 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) CATECHOL

PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.65g of the acid and 1.3g of catechol in an oil bath at 120-130 °C for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of (2-hydroxy-5-methylphenyl) phenol phthal-as-ein. Yield 1.3g.

The black dye having a m.p. > 360 °C is soluble in benzene, ethanol, methanol and acetic acid. It yields a brown colour in ethanol that turns to brownish black on adding a drop of an alkali.

Anal. For.: C₂₁H₁₆O₅ (Mol. Wt. 348)

Calc. : C, 72.41; H, 4.60

Found : C, 72.31; H, 4.57

3.1.3 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) RESORCINOL

PHTHAL-AS-EIN:

It was prepared by the condensation of 5.0g of the acid and 2.6g of resorcinol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid for about four and half-hours. The condensed mass was crushed and washed with an excess of water to remove excess of resorcinol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was filtered from the reddish brown with green fluorescent filtrate by slowly gradual addition of dilute hydrochloric acid accompanied by constant stirring. The dye was purified by crystallization from rectified spirit, dried in an oven at 100 °C and then in a vacuum dessicator. Yield 2.8g.

The dark orange dye having a m.p. 290-292 °C is soluble in benzene, ethanol and methanol. It dissolves in ethanol giving a golden yellow colour with green fluorescence on adding a drop of an alkali.

Anal. For.: $C_{21}H_{16}O_5$ (Mol. Wt. 348)

Calc. : C, 72.41; H, 4.60

Found : C, 72.33; H, 4.58

3.1.4 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL)

HYDROQUINONE PHTHAL-AS-EIN:

1.5g of the acid and 1.2g of hydroquinone were treated in an oil bath at 160-180 °C for four hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described earlier.

Yield 1.5g.

The black coloured dye, decomposing at 320 °C is soluble in ethanol, methanol, chloroform and acetic acid. Its ethanolic solution is crimson in colour that turns into dark brown on the addition of a drop of an alkali.

Anal. For.: $C_{21}H_{16}O_5$ (Mol. Wt. 348)

Calc. : C, 72.41; H, 4.60

Found : C, 72.34; H, 4.56

3.1.5 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) PYROGALLOL

PHTHAL-AS-EIN:

The mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein. Yield 1.8g.

The black coloured dye (m.p. >360 °C) yields wine red colour in ethanol that turns into blue violet on adding a drop of an alkali.

Anal. For. : $C_{21}H_{16}O_6$ (Mol. Wt. 364)

Calc. : C, 69.23; H, 4.40

Found : C, 69.17; H, 4.38

3.1.6 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL)

PHLOROGLUCINOL PHTHAL-AS-EIN:

The mixture of 1.5g of the acid, 1.2g of phluroglucinol along with a few drops of concentrated sulphuric acid were together heated on an oil bath at 190-200 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein. Yield 2.2g.

The orange coloured dye (m.p. 320-322 °C) yields a yellow coloured solution in ethanol that turns dark red on adding a drop of an alkali.

Anal. For. : $C_{21}H_{16}O_6$ (Mol. Wt. 364)

Calc. : C, 69.23; H, 4.40

Found : C, 69.18; H, 4.37

3.1.7 ACETYLATION OF (2-HYDROXY-5-METHYLPHENYL) RESORCINOL

PHTHAL-AS-EIN:

[(2-ACETOXY-5-METHYLPHENYL) DIACETYL RESORCINOL PHTHAL-AS-EIN]

1.0g of the dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 125-135 °C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a light yellow solid settled down. It was filtered, washed well and dried. The yellow acetyl derivative was treated with animal charcoal and finally crystallised from aqueous ethanol in presence of a drop of acetic acid. Yield 0.8g.

The yellow coloured triacetyl derivative (m.p. 188-189 °C) is soluble in benzene, ethanol, methanol, chloroform and acetic acid.

Anal. For. : $C_{27}H_{22}O_8$ or $C_{21}H_{13}O_5(OC.CH_3)_3$ (Mol. Wt. 474)

Calc. : C, 68.35; H, 4.64; acetyl, 27.22

Found : C, 68.28; H, 4.61; acetyl, 27.15

3.1.8 BROMINATION OF (2-HYDROXY-5-METHYLPHENYL)

RESORCINOLPHTHAL-AS-EIN:

[(3-bromo-2-hydroxy-5-methylphenyl) dibromo resorcinol phthal-as-ein]

The 1.0-g of the dye (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess

of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 80 °C in an oven and then in a vacuum dessicator. Yield 0.82g.

The orange crystalline dye having m.p. 250-251 °C is soluble in benzene ether, chloroform and acetone. Its ethanolic solution is red in colour, which turns into reddish pink with green fluorescence on addition of an alkali.

Anal. For. : $C_{21}H_{13}Br_3O_5$ (Mol. Wt. 585)

Calc. : Br, 41.03

Found : Br, 40.95

3.1.9 CAUSTIC POTASH TREATMENT OF (2-HYDROXY-5-

METHYLPHENYL) RESORCINOL PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four hours till the dark colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II), which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone, m.p. 182-183 °C. It gave positive tests for carboxyl and phenolic groups and was identified and confirmed as o- (2-hydroxy-

5-methylbenzoyl) benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

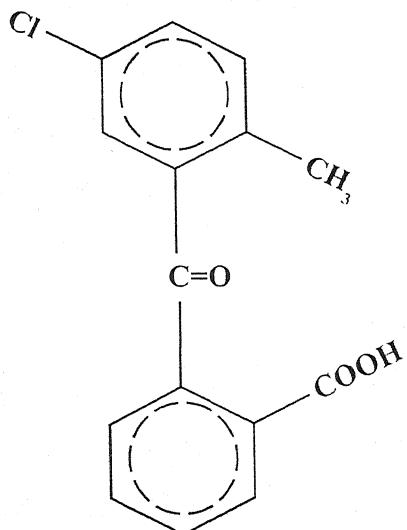
The purified residue melted at 108-109 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart A.

A. 2

3.2 DYES DERIVED FROM 2-(5'-CHLORO-2'-METHYLBENZOYL) BENZOIC

ACID:



2-(5'-chloro-2'-methylbenzoyl) benzoic acid

Figure 3.03

3.2A PREPARATION OF 2-(5'-CHLORO-2'-METHYLBENZOYL) BENZOIC

ACID:

Friedel Craft's reactions between 80ml of AR dry para-chlorotoluene and 14.6g (about 0.1 mole) of phthalic anhydride in presence of 27g of anhydrous aluminium chloride (about 0.2 mole) as catalyst to prepare the acid¹⁻³. The yield was found to be 18.2g. The excess of para-chlorotoluene was used for the purpose of a solvent. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a reflux condenser connected with a gas absorption trap. The reaction was carried out below 20°C by adding anhydrous aluminium chloride in small portions. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until the evolution of hydrogen chloride ceased for all practical purposes.

Adding 25ml of concentrated hydrochloric acid in about 200ml of ice cold water decomposed the heavy dark coloured complex. The excess of para-chlorotoluene

was removed by steam distillation. The residue was extracted three four times with hot boiling 10% solution of sodium carbonate and filtered. The acid was precipitated from the filtrate by gradual addition of concentrated hydrochloric acid. It was filtered off, washed well with cold water, dried and recrystallised from methanol(m.p. 181-183°C. The white needle shaped crystalline acid is soluble in hot water, methanol, ethanol, chloroform and acetone.

Anal. For.: $C_{15}H_{11}ClO_3$ (Mol. Wt. 274.5)

Calc. : C, 65.57; H, 4.01; Cl, 12.93

Found : C, 65.52; H, 4.00; Cl, 12.91

3.2B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.6 g of fused sodium acetate was refluxed with 18 ml of freshly distilled acetic anhydride at 120-130 °C for about four hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of a light brown solid, m.p. 268-270 °C. It is soluble in acetone, chloroform and acetic acid. Yield 0.70 g.

Anal. For.: $C_{17}H_{13}ClO_4$ or $C_{15}H_{10}ClO_3(OC.CH_3)$ (Mol. Wt. = 316.5)

Calc. : C, 64.45; H, 4.11; Cl, 11.22; acetyl. 13.59

Found : C, 64.36; H, 4.10; Cl, 11.20; acetyl. 13.57

The dyes prepared from the acid may be represented by the following structures:

PLEASE TURN OVER

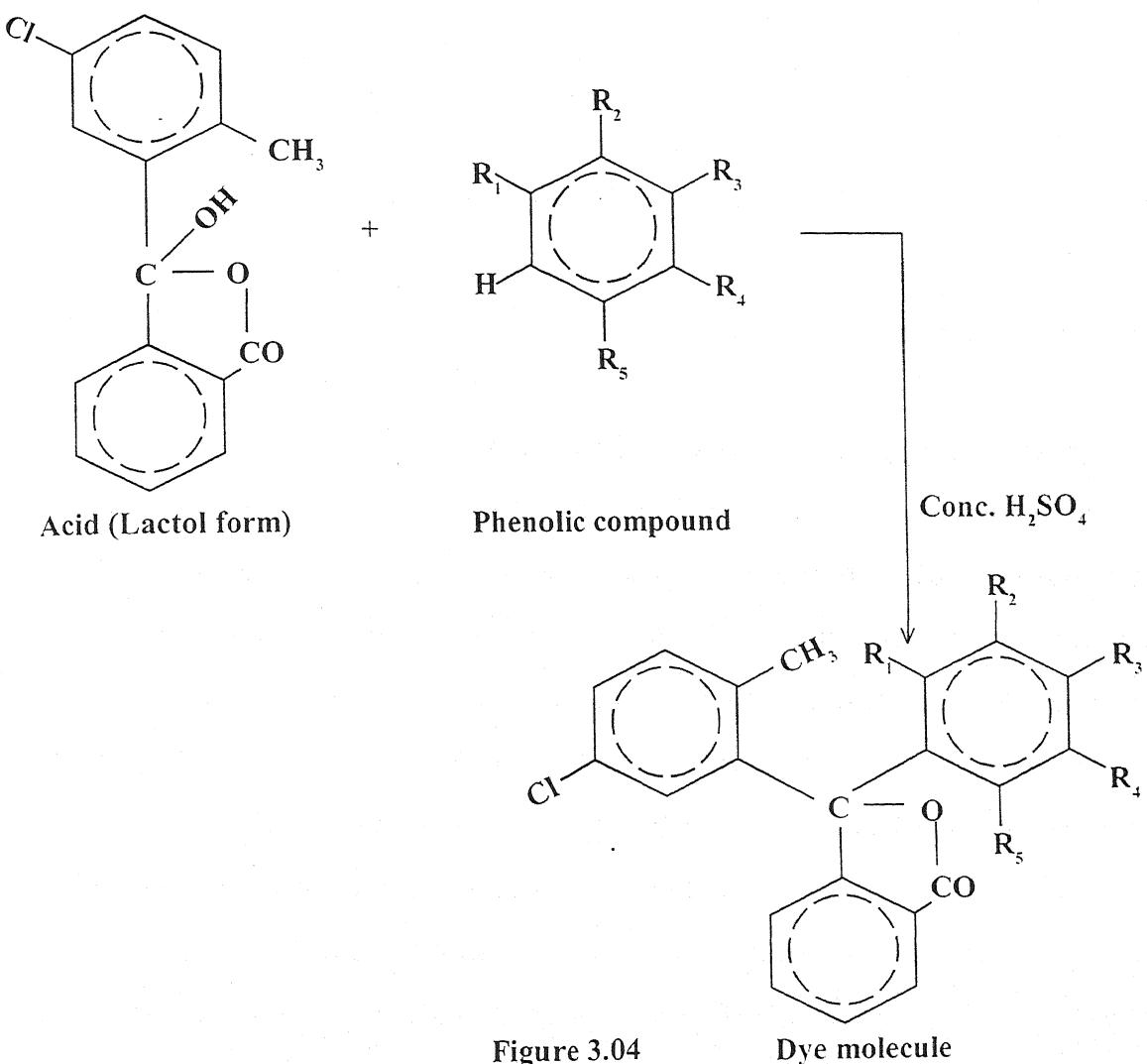
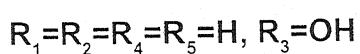


Figure 3.04

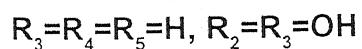
Dye molecule

DYES:

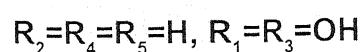
3.2.1 (5-chloro-2-methylphenyl) phenol phthal-as-ein:



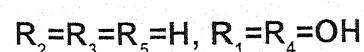
3.2.2 (5-chloro-2-methylphenyl) catechol phthal-as-ein:



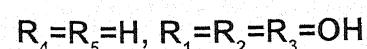
3.2.3 (5-chloro-2-methylphenyl) resorcinol phthal-as-ein:



3.2.4 (5-chloro-2-methylphenyl) hydroquinone phthal-as-ein:



3.2.5 (5-chloro-2-methylphenyl) pyrogallol phthal-as-ein:



3.2.6 (5-chloro-2-methylphenyl) phloroglucinol phthal-as-ein:

$$R_2 = R_4 = H, R_1 = R_3 = R_5 = OH$$

3.2.7 (5-chloro-2-methylphenyl) diacetyl resorcinol phthal-as-ein:

$R_2 = R_4 = R_5 = H, R_1 = R_3 = 0.C0.CH_3$

3.2.8 (2-hydroxy-5-methylphenyl) dibromo resorcinol phthal-as-ein:

$R_5 = H, R_1 = R_3 = OH, R_2 = R_4 = Br$

3.2.1 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) PHENOL PHTHAL-

A homogeneous mixture of 2.5 g of the acid and 2.0 g of phenol was first heated at 120 °C to make it homogeneous and then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-170°C for about five and a half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The buff coloured solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the buff coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 2.0g, m.p. 142-144 °C.

The pinkish red buff coloured dye is soluble in ethanol and rectified spirit. The ethanolic solution of the dye is almost brownish red in colour which turns into pink on adding a drop of an alkali. In strong basic medium, it gives pink colour. The purity of the dye was tested by paper chromatography adopting technique 1A.1B.

Mobile phase Butanol saturated with ammonia

Developing agent 1% aqueous caustic soda

Reference dye Phenolphthalein

A 25-cm X10 cm strip of Whatman filter paper was cut and a very dilute solution was spotted with a microsyringe on a base line 4.0-cm from the bottom end. Similarly, a very dilute aqueous solution of the reference dye was also spotted 3.0

cm away from the first spot on the base line. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed with the developing agent. The developed chromatogram revealed only one spot for each of the two dyes. This was enough to confirm the homogeneity and purity of the dye.

Found R_f (Phenolphalein): 0.93

R_f ((5-chloro-2-methylphenyl) phenol phthal-as-ein: 0.94

Reported R_f (Phenolphthalein) 0.92

Anal. For.: $C_{21}H_{15}ClO_3$ (Mol. Wt. 350.5)

Calc. : C, 71.90; H, 4.28; Cl, 10.13

Found : C, 71.85; H, 4.26; Cl, 10.11

3.2.2 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) CATECHOL

PHTHAL-AS-EIN:

It was prepared by the condensation of 2.0g of the acid and 1.5g of catechol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid for about four hours at 125-135°C. The condensed mass was crushed and washed with an excess of water to remove excess of catechol. It was extracted with 2% aqueous solution of caustic soda and filtered. The dye was filtered from the reddish brown with green fluorescent filtrate by slowly gradual addition of dilute hydrochloric acid accompanied by constant stirring. The dye was purified by crystallisation from rectified spirit, dried in an oven at 100°C and then in a vacuum dessicator. Yield 1.2g.

The black dye has a m.p. 360°C. It dissolves in ethanol giving a brown coloured solution that changes to black on adding a drop of an alkali.

Anal. For.: $C_{21}H_{15}ClO_4$ (Mol. Wt. 366.5)

Calc. : C, 68.76; H, 4.09; Cl, 9.69

Found : C, 68.70; H, 4.06; Cl, 9.5

3.2.3 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 4.5g of the acid and 3.0g of resorcinol in an oil bath at 145-160 °C for four hours in presence of a few drops of concentrated sulphuric acid. The condensed solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the reddish brown with green fluorescence extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated recrystallisation from rectified spirit and dried at 100 °C and then in vacuum in a dessicator. Yield 2.5g.

The dye is red, crystalline in nature having a m.p. 278-279 °C. It yields a golden yellow colour with fluorescence in ethanol which turns to reddish yellow with green fluorescence on adding a drop of an alkali.

Anal. For.: $C_{21}H_{15}ClO_4$ (Mol. Wt. 366.5)

Calc. : C, 68.76; H, 4.09; Cl 9.69

Found : C, 68.74; H, 4.08; Cl 9.65

3.2.4 PREPARATION OF (5-CHLORO-2-METHYLPHENYL)

HYDROQUINONE PHTHAL-AS-EIN:

1.5g of the acid and 1.2g of hydroquinone was ground into a mixture and was treated in an oil bath at 160-175 °C for four hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 5-chloro-2-methylphenyl resorcinol phthal-as-ein described earlier. Yield 1.5g.

The black coloured crystalline dye, decomposing above 300 °C is soluble in ethanol, methanol, chloroform and acetic acid. Its ethanolic solution is golden brown in colour that turns into leaf brown on the addition of a drop of an alkali.

Anal. For.: $C_{21}H_{15}ClO_4$ (Mol. Wt. 366.5)

Calc. : C, 68.76; H, 4.09; Cl 9.69

Found : C, 68.70; H, 4.07; Cl 9.65

3.2.5 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) PYROGALLOL

PHTHAL-AS-EIN:

The mixture of 1.2g of the acid and 1.0g of pyrogallol were mixed to make a homogeneous mass and the condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 130-150 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 5-chloro-2-methylphenyl resorcinol phthal-as-ein. Yield 0.8g.

Anal. For.: $C_{21}H_{15}ClO_5$ (Mol. Wt. 382.5)

Calc. : C, 65.88; H, 3.92; Cl, 9.28

Found : C, 65.75; H, 3.90; Cl, 9.25

3.2.6 PREPARATION OF (5-CHLORO-2-METHYLPHENYL)

PHLOROGLUCINOL PHTHAL-AS-EIN:

The mixture of 1.2g of the acid, 1.0g of phluroglucinol were mixed intimately to make a homogeneous mixture and along with a few drops of concentrated sulphuric acid as condensing agent was heated on an oil bath at 130-150 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for 5-chloro-2-methylphenyl resorcinol phthal-as-ein. Yield 0.9g.

The dark orange dye (m.p. >360 °C yields a golden yellow coloured solution in ethanol that turns reddish orange on adding a drop of an alkali.

Anal. For.: $C_{21}H_{15}ClO_5$ (Mol. Wt. 382.5)

Calc. : C, 65.88; H, 3.92; Cl, 9.28

Found : C, 65.78; H, 3.90; Cl, 9.25

3.2.7 ACETYLATION OF (5-CHLORO-2-METHYLPHENYL)

RESORCINOLPHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIACETYL RESORCINOL PHTHAL-AS-EIN]

1.0g of the dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser.

The contents were refluxed at 125-135 °C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a light yellow solid settled down. It was filtered, washed well and dried. The yellow acetyl derivative was treated with animal charcoal and finally crystallised from aqueous ethanol in presence of a drop of acetic acid. It was dried in an oven at 40 °C and then over phosphorous pentaoxide under reduced pressure. Yield 0.65g.

The pale yellow coloured diacetyl derivative (m.p. 175-176 °C) which has a microcrystalline nature is soluble in ethanol, methanol, chloroform and acetic acid.

Anal. For.: $C_{21}H_{15}ClO_6$ or $C_{21}H_{13}ClO_4(OC.CH_3)_2$ (Mol. Wt. 450.5)

Calc. : C, 66.59; H, 4.22; Cl, 7.88; acetyl, 19.09

Found : C, 66.52; H, 4.20; Cl, 7.85; acetyl, 19.06

3.2.8 BROMINATION OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

PHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIBROMO RESORCINOL PHTHAL-AS-EIN]

The 1.5-g of the dye 5-chloro-2-methylphenyl resorcinol phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was slowly and gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in a dilute aqueous solution of caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 80 °C in an oven and then in a vacuum dessicator. Yield 1.2g.

The pale orange crystalline dye having m.p. 252-253 °C is soluble in methanol, ethanol, acetic acid and acetone.

Anal. For.: $C_{21}H_{13}Br_2ClO_5$ (Mol. Wt. 524.5)

Calc. : Br, 30.50

Found : Br, 30.48

3.2.9 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-METHYLPHENYL)

RESORCINOL PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated in a sand bath with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four hours till the dark red colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark red residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II) that was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions of the dye itself and melting point determination with the original sample of the dye.

Identification of the residue II:

It was recrystallised from acetone, m.p. 181-183 °C. It gave positive tests for carboxyl group and was identified and confirmed as 2-(5'-chloro-2'-methybenzoyl) benzoic acid by mixed melting point determination and superimposition of IR spectra with that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, Tollen's reagent and gave fluorescein test

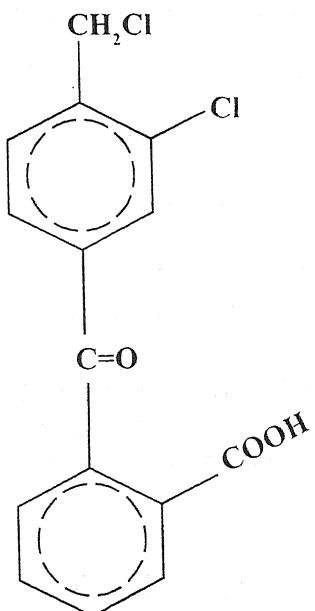
with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. It was further confirmed by mixed melting point determination with the authentic sample of resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart B.

A.3

3.3 DYES DERIVED FROM 2-(3'-CHLORO-4'CHLOROMETHYLBENZOYL)

BENZOIC ACID:



2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid

Figure 3.05

3.3A PREPARATION OF 2-(3'-CHLORO-4'-CHLOROMETHYLBENZOYL)

BENZOIC ACID:

The acid¹ was prepared by the Friedel Craft's reaction between 100ml of AR dry o-chlorobenzyl chloride and 15.0g (about 0.1 mole) of phthalic anhydride in presence of 27g of anhydrous aluminum chloride (about 0.2 mole) as catalyst in a similar manner as 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid. The acid was crystallised from hot water in the form of a white crystalline solid with m.p. 184-185 °C. The acid was found to be soluble in methanol and sparingly soluble in acetone. The yield was found to be 19.2g.

Anal. For. : $C_{15}H_{10}Cl_2O_3$ (Mol. Wt. 309)

Calc. : C, 58.25; H, 3.24; Cl, 22.98

Found : C, 58.22; H, 3.23; Cl, 22.96

3.3B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

It was prepared by taking 1.0 g of the acid and 3.0 g of fused sodium acetate

and refluxing them with 15 ml of freshly distilled acetic anhydride at 120-130°C in a similar manner as in the case of acetyl derivative of 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid. The acetyl derivative settled down in the form of a coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was recrystallised from acetone in the form of a light brown solid, m.p. 124-125°C. It is soluble in acetone, chloroform, ethanol and acetic acid. Yield 0.68 g.

Anal. For. : $C_{17}H_{12}Cl_2O_4$ (Mol. Wt. = 351)

Calc. : C, 58.12; H, 3.42; Cl, 20.23; acetyl. 12.25

Found : C, 58.02; H, 3.40; Cl, 20.19; acetyl. 12.23

The dyes prepared from the acid may be represented by the following structures: CH_2Cl

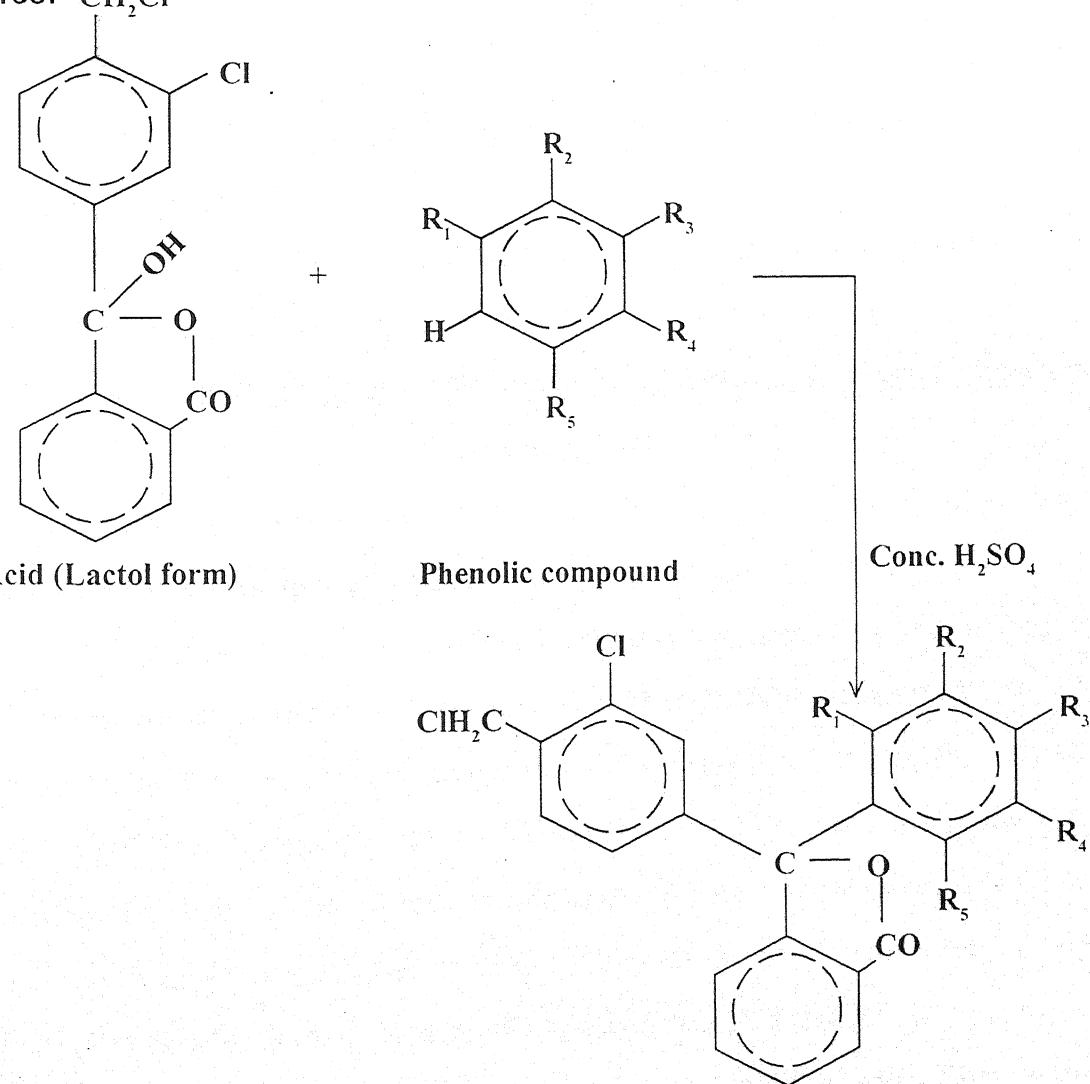
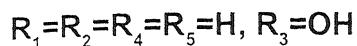


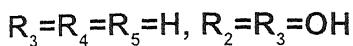
Figure 3.06

DYES:

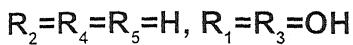
3.3.1 (3-chloro-4-chloromethylphenyl) phenol phthal-as-ein:



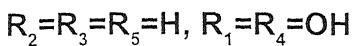
3.3.2 (3-chloro-4-chloromethylphenyl) catechol phthal-as-ein:



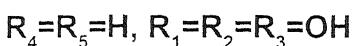
3.3.3 (3-chloro-4-chloromethylphenyl) resorcinol phthal-as-ein:



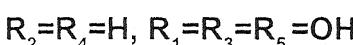
3.3.4 (3-chloro-4-chloromethylphenyl) hydroquinone phthal-as-ein:



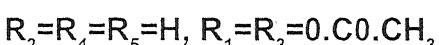
3.3.5 (3-chloro-4-chloromethylphenyl) pyrogallol phthal-as-ein:



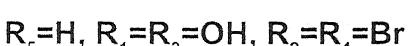
3.3.6 (3-chloro-4-chloromethylphenyl) phloroglucinol phthal-as-ein:



3.3.7 (3-chloro-4-chloromethylphenyl) diacetyl resorcinol phthal-as-ein:



3.3.8 (3-chloro-4-chloromethylphenyl) dibromo resorcinol phthal-as-ein:



3.3.1 PREPARATION OF (3-chloro-4-chloromethylphenyl) phenol phthal-as-

ein:

A homogenised intimate mixture of 1.5 g of the acid and 1.0 g of phenol was condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 165-175 °C for about four hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The buff coloured solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 1.5g, m.p. 113-115 °C.

The dark brown coloured dye is soluble in ethanol and rectified spirit. The ethanolic

solution of the dye is almost reddish cream in colour which turns into pink on adding a drop of an alkali. In strong basic medium, it gives pink colour.

Anal. For.: $C_{21}H_{14}Cl_2O_3$ (Mol. Wt. 385)

Calc. : C, 65.45; H, 3.64; Cl, 18.44

Found : C, 65.42; H, 3.62; Cl, 18.42

3.3.2 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

CATECHOL PHTHAL-AS-EIN:

It was prepared by the condensation of 1.0g of the acid and requisite amount of catechol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid for about three and half hours at 125-135 °C. The condensed mass was crushed and washed with an excess of water to remove excess of catechol. It was isolated and purified as done for the corresponding phenol dye. Yield 0.8g

The black powdery dye having a m.p. > 360 °C. It dissolves in ethanol giving a brownish black coloured solution that darkens on adding a drop of an alkali.

Anal. For.: $C_{21}H_{14}Cl_2O_4$ (Mol. Wt. 401)

Calc. : C, 62.84; H, 3.49; Cl, 17.71

Found : C, 62.82; H, 3.48; Cl, 17.67

3.3.3 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

RESORCINOL PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 5.0g of the acid and 3.0g of resorcinol in an oil bath at 135-145 °C for four hours in presence of a few drops of concentrated sulphuric acid. The condensed brittle solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the reddish brown with green fluorescent extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated recrystallisation from rectified spirit and dried at 100 °C and then in vacuum in a dessicator. Yield 5.4g.

The dye is red, crystalline in nature having a m.p. 278-279 °C. It yields a golden yellow colour with fluorescence in ethanol which turns to reddish yellow with

green fluorescence on adding a drop of an alkali.

Anal. For.: $C_{21}H_{14}Cl_2O_4$ (Mol. Wt. 401)

Calc. : C, 62.84; H, 3.49; Cl, 17.71

Found : C, 62.82; H, 3.48; Cl, 17.68

3.3.4 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

HYDROQUINONE PHTHAL-AS-EIN:

1.0g of the acid and 1.0g of hydroquinone was ground into an intimate mixture and was treated in an oil bath at 160-175 °C for four hours in presence of four five drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 5-chloro-2-methylphenyl resorcinol phthal-as-ein described earlier. Yield 0.85g.

The black coloured powdery dye, decomposing above 360 °C is soluble in ethanol, methanol, chloroform and acetic acid. Its ethanolic solution is brown in colour that turns into blackish brown on the addition of a drop of an alkali.

Anal. For.: $C_{21}H_{14}Cl_2O_4$ (Mol. Wt. 401)

Calc. : C, 62.84; H, 3.49; Cl, 17.71

Found : C, 62.80; H, 3.47; Cl, 17.68

3.3.5 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

PYROGALLOL PHTHAL-AS-EIN:

The intimate and homogeneous mixture of 1.0g of the acid and 1.0g of pyrogallol were mixed to make a homogeneous mass and the condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 135-145 °C for about four hours till the melt became hard and brittle. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 5-chloro-2-methylphenyl resorcinol phthal-as-ein. Yield 0.8g.

Anal. For.: $C_{21}H_{14}Cl_2O_5$ (Mol. Wt. 417)

Calc. : C, 60.43; H, 3.36; Cl, 17.03

Found : C, 60.40; H, 3.35; Cl, 17.00

3.3.6 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

PHLOROGLUCINOL PHTHAL-AS-EIN:

The homogeneous mixture of 1.0g of the acid, 1.0g of phluroglucinol were mixed intimately to make a homogeneous mixture and along with a few drops of concentrated sulphuric acid as condensing agent was heated on an oil bath at 200-220 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for 5-chloro-2-methylphenyl resorcinol phthal-as-ein. Yield 0.80g.

The reddish brown dye m.p. 180 °C (decomp.) yields a golden yellow coloured solution in ethanol that turns dark red on adding a drop of an alkali.

Anal. For.: $C_{21}H_{14}Cl_2O_5$ (Mol. Wt. 417)

Calc. : C, 60.43; H, 3.36; Cl, 17.03

Found : C, 60.38; H, 3.34; Cl, 17.00

3.3.7 ACETYLATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

RESORCINOL PHTHAL-AS-EIN:

[(3-CHLORO-4-CHLOROMETHYLPHENYL) DIACETYL RESORCINOL

PHTHAL-AS-EIN]

1.0g of the dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 130-140 °C for about four hours. The hot contents were poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a light yellow solid settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and finally crystallised from aqueous ethanol in presence of a drop of acetic acid. It was dried in an oven at 70 °C and then over phosphorous pentaoxide under reduced pressure. Yield 0.75g.

The pale yellow coloured diacetyl derivative (m.p. 182-184 °C) is soluble in ethanol, methanol, chloroform and acetic acid.

Anal. For. : $C_{25}H_{18}Cl_2O_6$ or $C_{21}H_{12}Cl_2O_4(OC.CH_3)_2$ Mol. Wt. 485

Calc. : C, 61.86; H, 3.71; Cl, 14.64; acetyl, 17.73

Found : C, 61.80; H, 3.70; Cl, 14.62; acetyl, 17.71

3.3.8 BROMINATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

RESORCINOL PHTHAL-AS-EIN:

[PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL) DIBROMO

RESORCINOL PHTHAL-AS-EIN]

The 1.0-g of the dye 3-chloro-4-chloromethylphenyl resorcinol phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was slowly and gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dark orange substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in a dilute aqueous solution of caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110 °C in an oven and then in a vacuum dessicator. Yield 0.92g.

The dark orange crystalline dye having m.p. 290-292°C is soluble in methanol, ethanol and acetone.

Anal. For. : $C_{21}H_{12}Br_2Cl_2O_4$ (Mol. Wt. 559)

Calc. : Br, 28.62

Found : Br, 28.61

3.3.9 CAUSTIC POTASH TREATMENT OF (3-CHLORO-4-CHLOROMETHYLPHENYL) RESORCINOL PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated in a sand bath with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about three and a half

hours till the colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark orange residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II) that was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a dark orange residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from the colour reactions of the dye itself and melting point determination with the original sample of the dye.

Identification of the residue II:

It was recrystallised from acetone (m.p.184-185 °C). It gave positive tests for carboxyl group and was identified and confirmed as 2- (3'-chloro-4'-chloromethylbenzoyl) benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-111 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, Tollen's reagent and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol. It was further confirmed by mixed melting point determination with the authentic sample of resorcinol.

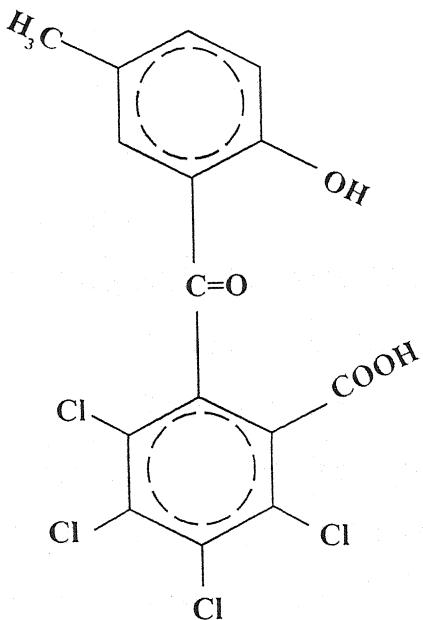
Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart C.

B.1

3.4 DYES DERIVED FROM 2-(2'HYDROXY-5'-METHYLBENZOYL)

TETRACHLORO BENZOIC ACID:



2-(2'-hydroxy-5'-methylbenzoyl)tetrachlorobenzoic acid

Figure 3.07

3.4A PREPARATION OF 2-(2'HYDROXY-5'-METHYLBENZOYL)

TETRACHLORO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between p-cresol (dry AR, 85 ml) and tetrachloro phthalic anhydride (28.5 g, about 0.1 mole) and anhydrous AlCl_3 (27.0g, about 0,2 moles) was used as a catalyst. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 35°C by adding AlCl_3 in installments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until evaporation of HCl ceased.

The heavy dark coloured complex was decomposed by the addition of 30ml concentrated hydrochloric acid in 250ml-ice cold water. The excess of ethylbenzene was removed by distillation. The residue was extracted three four times with boiling 10 % solution of sodium carbonate and filtered. The acid was

precipitated from the filtrate by the gradual addition of concentrated sulphuric acid. It was filtered off, washed well with cold water, dried and crystallised from acetone. It had a melting point of 230-231 °C. It was found to be soluble in water, acetone and methanol. Yield 20.0 g.

Anal. For.: $C_{15}H_8Cl_4O_4$ (Mol. Wt. = 394)

Calc. : C, 45.69; H, 2.03; Cl, 36.04

Found : C, 45.61; H, 2.02; Cl, 36.02.

3.4B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.5 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 120-130 °C for about four hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of a brown solid, m.p. 202-203 °C. It is soluble in benzene, acetone, chloroform and acetic acid. Yield 0.78 g.

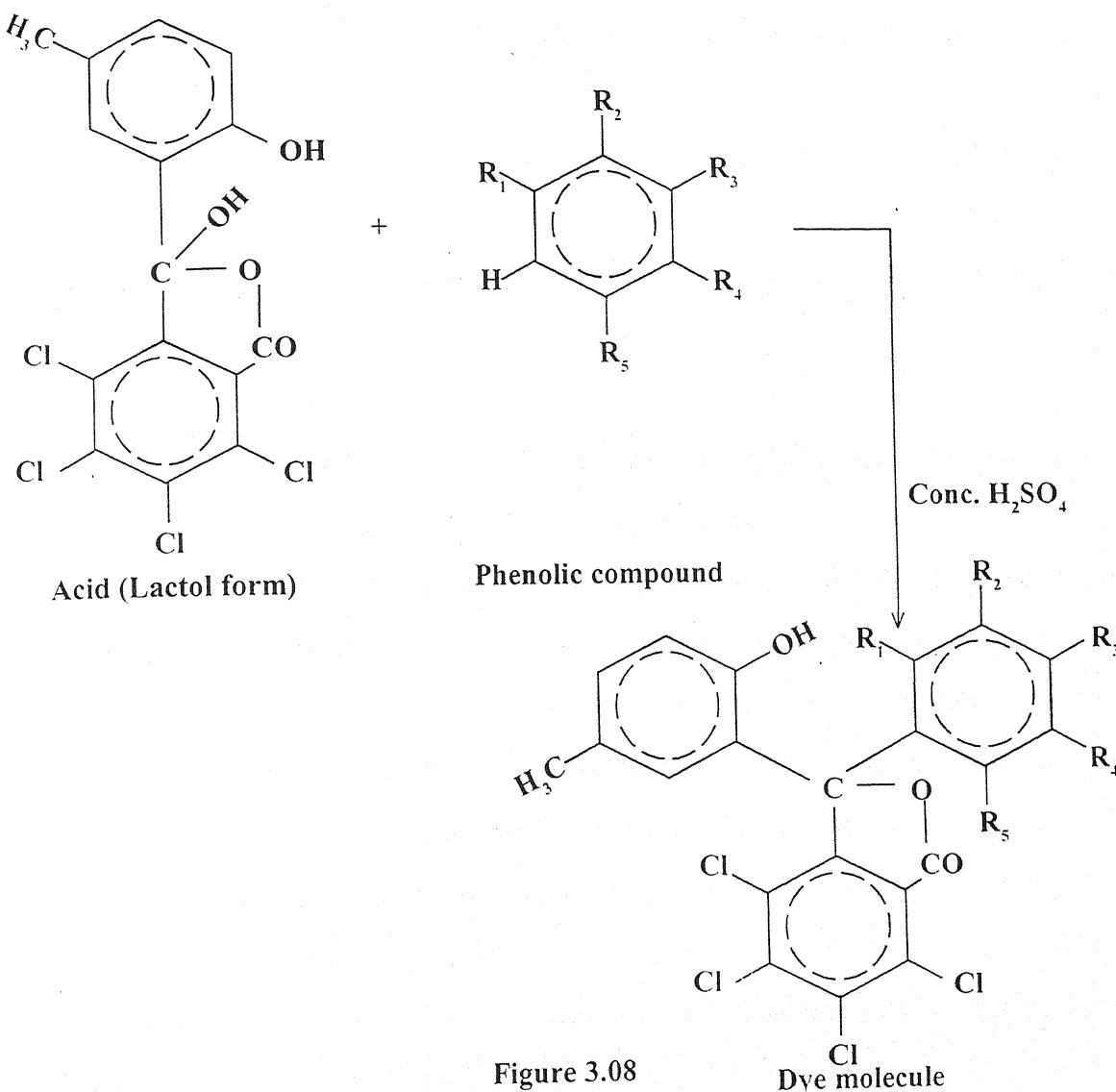
Anal. For.: $C_{19}H_{12}Cl_4O_6$ or $C_{15}H_6Cl_4O_4(OC.CH_3)_2$ (Mol. Wt. = 478)

Calc. : C, 47.70; H, 2.51; Cl, 29.71 acetyl. 17.99

Found : C, 47.62; H, 2.49; Cl, 29.68 acetyl. 17.96

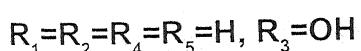
The dyes prepared from the acid may be represented by the following structures:

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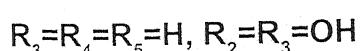


DYES:

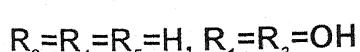
3.4.1 2-hydroxy-5-methylphenyl phenol tetrachloro phthal-as-ein:



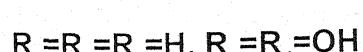
3.4.2 2-hydroxy-5-methylphenyl catechol tetrachloro phthal-as-ein:



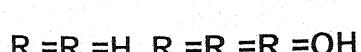
3.4.3 2-hydroxy-5-methylphenyl resorcinol tetrachloro phthal-as-ein:



3.4.4 2-hydroxy-5-methylphenyl hydroquinone tetrachloro phthal-as-ein:



3.4.5 2-hydroxy-5-methylphenyl pyrogallol tetrachloro phthal-as-ein:



3.4.6 2-hydroxy-5-methylphenyl phloroglucinol tetrachloro phthal-as-ein:

$R_2=R_4=H$, $R_1=R_3=R_5=OH$

3.4.7 2-acetoxy-5-methylphenyl diacetyl resorcinol tetrachloro phthal-as-ein:

$R_2=R_4=R_5=H$, $R_1=R_3=O.C0.CH_3$

3.4.8 3-bromo-2-hydroxy-5-methylphenyl dibromo resorcinol tetrachloro phthal-as-ein:

$R_5=H$, $R_1=R_3=OH$, $R_2=R_4=Br$

3.4.1 PREPARATION OF (2-hydroxy-5-methylphenyl) phenol

TETRACHLORO phthal-as-ein:

A homogenized intimate mixture of 1.5 g of the acid and 1.0 g of phenol was condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-170 °C for about four hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The reddish pink solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 1.3g.

The pinkish reddish orange dye has a m.p. 220-222 °C. The ethanolic solution of the dye is light yellow in colour that turns into pink on adding a drop of an alkali. In strong basic medium, it gives intense pink colour.

Anal. For.: $C_{21}H_{12}Cl_4O_4$ (Mol. Wt. 470)

Calc. : C, 53.62; H, 2.55; Cl, 30.21

Found : C, 53.54; H, 2.51; Cl, 30.18

3.4.2 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) CATECHOL

TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.5g of the acid and 1.0g of catechol in an oil bath at 120-130 °C for four and half-hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were

done in a manner similar to that in the case of (2-hydroxy-5-methylphenyl) phenol phthal-as-ein described in subsection 3.1.1. Yield 1.2g.

The black coloured dye having a m.p. 242-243 °C is soluble in acetone, ethanol and acetic acid. It yields a golden brown colour in ethanol that turns to brown on adding a drop of an alkali.

Anal. For.: $C_{21}H_{12}Cl_4O_5$ (Mol. Wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22

Found : C, 51.78; H, 2.45; Cl, 29.19

3.4.3 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL

RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by the condensation of 4.0g of the acid and 3.5g of resorcinol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 140-160 °C for about four and half-hours. It was isolated and purified as described for 2-hydroxy-5-methylphenyl catechol tetrachloro phthal-as-ein earlier in the chapter.

Yield 3.0g

The greenish brown dye having a m.p. 280-281 °C is soluble in acetic acid, ethanol and methanol. It dissolves in ethanol giving a cream colour which turns into reddish orange with green fluorescence on adding a drop of an alkali.

Anal. For.: $C_{21}H_{12}Cl_4O_5$ (Mol. Wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22

Found : C, 51.76; H, 2.46; Cl, 29.18

3.4.4 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL)

HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180 °C for three and half-hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 1.2g.

The black dye, decomposing above 270 °C, is soluble in ethanol giving light brown colour that turns into dark brown on the addition of a drop of an alkali.

Anal. For.: $C_{21}H_{12}Cl_4O_5$ (Mol. Wt. 486)

Calc. : C, 51.85; H, 2.47; Cl, 29.22

Found : C, 51.78; H, 2.45; Cl, 29.19

3.4.4 PREPARATION OF (2-HYDROXY-5-METHYLPHENYL) PYROGALLOL

TETRACHLORO PHTHAL-AS-EIN:

The mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier. Yield 1.2g.

The black coloured dye having m.p. above 360 °C is soluble in acetone, alcohol and acetic acid. The ethanolic solution is dark brown in colour which on adding a drop of an alkali becomes blue.

Anal. For.: $C_{21}H_{12}Cl_4O_6$ (Mol. Wt. 502)

Calc. : C, 50.20; H, 2.39; Cl, 28.29

Found : C, 50.14; H, 2.37; Cl, 28.26

3.4.6 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL

PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.0g of phluroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 180-200 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.3 early in this chapter. Yield 1.2g.

The dark red coloured dye (m.p. 180 °C) yields a wine red coloured solution in ethanol that turns red with green fluorescence on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and in acetic acid.

Anal. For. : $C_{21}H_{12}Cl_4O_6$ (Mol. Wt. 502)

Calc. : C, 50.20; H, 2.39; Cl, 28.29

Found : C, 50.09; H, 2.35; Cl, 28.23

3.4.7 ACETYLATION OF (2-HYDROXY-5-METHYLPHENYL) RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

[(2-ACETOXY-5-METHYLPHENYL) DIACETYL RESORCINOL

TETRACHLORO PHTHAL-AS-EIN]

1.0g of the dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The acetylation, isolation and purification of the dye and the acetylated product was carried out in exactly the same manner as in the case of 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter. Yield 0.62g.

The golden brown coloured triacetyl derivative (m.p. 165-167 °C) is soluble in benzene, ether, chloroform and acetic acid.

Anal. For. : $C_{27}H_{18}Cl_4O_8$ or $C_{21}H_9Cl_4O_5(OC.CH_3)_3$ (Mol. Wt. 612)

Calc. : C, 52.94; H, 2.94; Cl, 23.20 acetyl, 21.08

Found : C, 52.86; H, 2.93; Cl, 23.16 acetyl, 21.04

3.4.8 BROMINATION OF (2-HYDROXY-5-METHYLPHENYL) RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

[(3-BROMO-2-HYDROXY-5-METHYLPHENYL) DIBROMO RESORCINOL

TETRACHLORO PHTHAL-AS-EIN]

The 1.0-g of the dye (2-hydroxy-5-methylphenyl) resorcinol tetrachloro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dirty orange substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of

excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 80°C in an oven and then in a vacuum dessicator. Yield 0.9g.

The brownish cream tinged dye having m.p. 315-317 °C is soluble in benzene, ether, chloroform and alcohol.

Anal. For.: $C_{21}H_9Br_3Cl_4O_5$ (Mol. Wt. 723)

Calc. : Br, 33.20

Found : Br, 33.14

3.4.9 CAUSTIC POTASH TREATMENT OF (2-HYDROXY-5-

METHYLPHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four hours till the dark colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II), which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. It gave positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(2'-hydroxy-5'-methylbenzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition

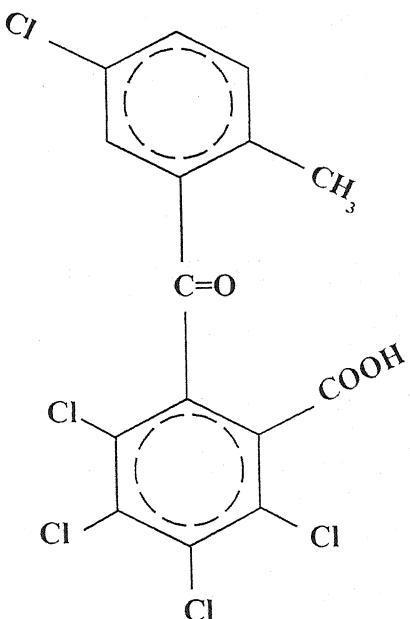
of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart A.

3.5 DYES DERIVED FROM 2-(5'CHLORO-2'-METHYLBENZOYL)TETRACHLORO BENZOIC ACID:

2-(5'-chloro-2'-methylbenzoyl)tetrachlorobenzoic acid

Figure 3.09

3.5APREPARATION OF 2-(5'-CHLORO-2'-METHYLBENZOYL)TETRACHLORO BENZOIC ACID:

The acid⁴⁻⁸ was prepared by carrying out Friedel Crafts reaction between parachlorotoluene (dry AR, 80 ml) and tetrachloro phthalic anhydride (28.0 g, about 0.1 mole) and anhydrous AlCl_3 (27.0g, about 0,2 moles) was used as a catalyst. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 25 °C by adding AlCl_3 in installments. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until evaporation of HCl ceased.

The heavy dark brown coloured complex was decomposed by the addition of 30ml concentrated hydrochloric acid in 250ml-ice cold water. The excess of parachlorotoluene was removed by distillation. The residue was extracted three four times with boiling 10 % solution of sodium carbonate and filtered. The acid

was precipitated from the filtrate by the gradual addition of concentrated sulphuric acid. It was filtered off, washed well with cold water, dried and crystallised from acetone. It had a melting point of 180 °C (dec.). The grey crystalline solid was found to be soluble in acetone and methanol. Yield 20.0 g.

Anal. For.: $C_{15}H_7Cl_5O_3$ (Mol. Wt. = 412.5)

Calc. : C, 43.64; H, 1.70; Cl, 43.03

Found : C, 43.62; H, 1.68; Cl, 43.01

3.5B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 120-130 °C for about four hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of a brown solid, decomposing at 114 °C. It is soluble in methanol, acetone, chloroform and acetic acid. Yield 0.62 g.

Anal. For.: $C_{17}H_9Cl_5O_4$ or $C_{15}H_6Cl_5O_3(OC.CH_3)$ (Mol. Wt. = 454.5)

Calc. : C, 44.88; H, 1.98; Cl, 39.05 acetyl. 9.46

Found : C, 44.85; H, 1.97; Cl, 39.00 acetyl. 9.43

The dyes prepared from the acid may be represented by the following structures:

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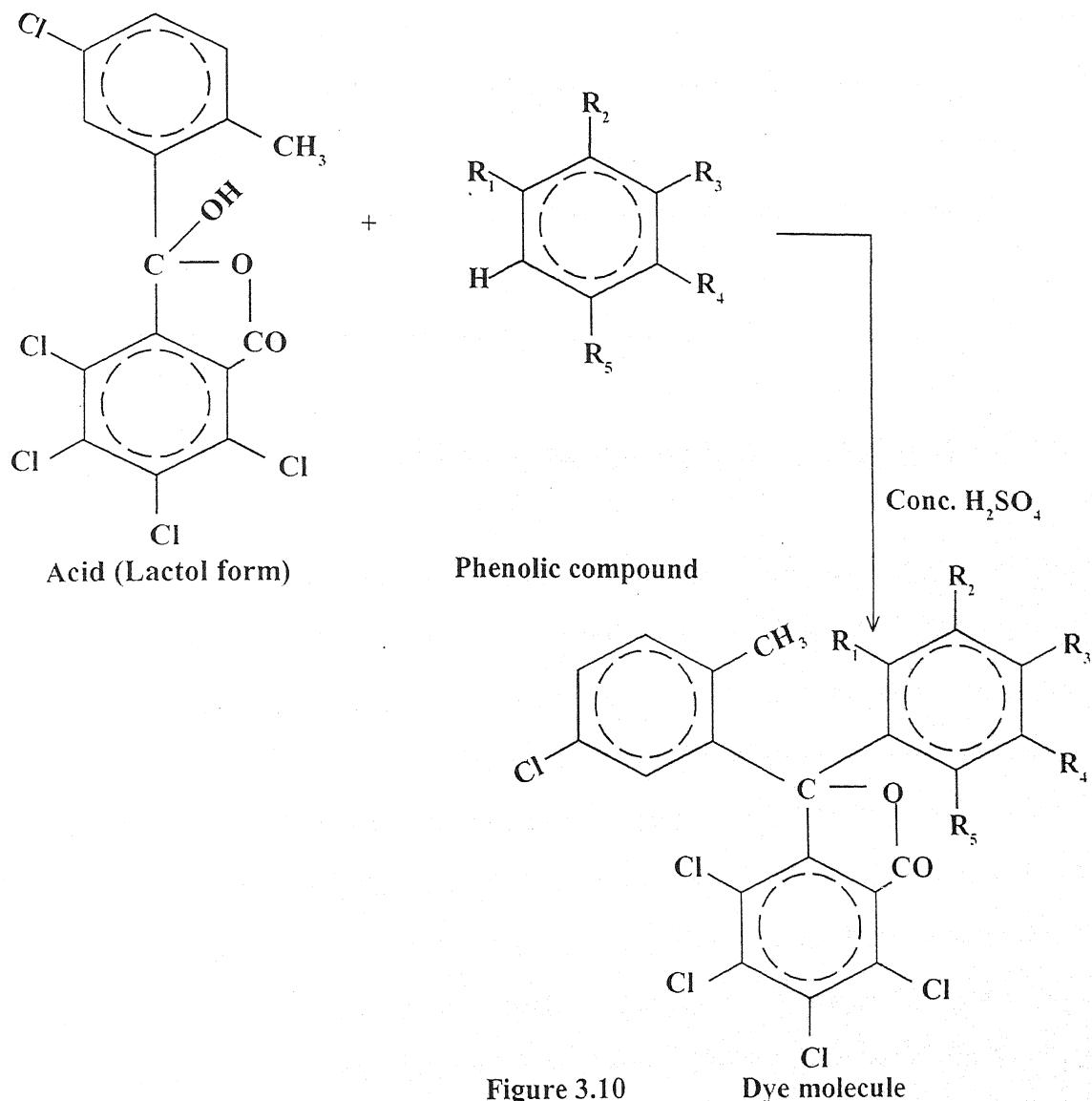
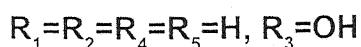


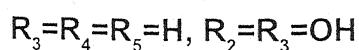
Figure 3.10

DYES:

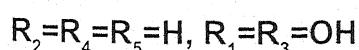
3.5.1 (5-chloro-2methylphenyl) phenol tetrachloro phthal-as-ein:



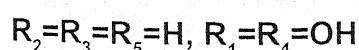
3.5.2 (5-chloro-2methylphenyl) catechol tetrachloro phthal-as-ein:



3.5.3 (5-chloro-2methylphenyl) resorcinol tetrachloro phthal-as-ein:



3.5.4 (5-chloro-2methylphenyl) hydroquinone tetrachloro phthal-as-ein:



3.5.5 (5-chloro-2methylphenyl) pyrogallol tetrachloro phthal-as-ein:

$$R_4 = R_5 = H, R_1 = R_2 = R_3 = OH$$

3.5.6 (5-chloro-2methylphenyl) phloroglucinol tetrachloro phthal-*as-ein*:

$$R_2 = R_4 = H, R_1 = R_3 = R_5 = OH$$

3.5.7(5-chloro-2methylphenyl) diacetyl resorcinol tetrachloro phthal-as-ein:

$R_2 = R_4 = R_5 = H, R_1 = R_3 = 0.C0.CH_3$

3.5.8 (5-chloro-2methylphenyl) dibromo resorcinol tetrachloro phthal-as-ein:

$R_5 = H, R_1 = R_3 = OH, R_2 = R_4 = Br$

3.5.1 PREPARATION OF (5-chloro-2-methylphenyl) phenol TETRACHLORO nthal-as-ein:

A homogenized intimate mixture of 1.5 g of the acid and 1.0 g of phenol (a slight excess than molecular proportion) was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175°C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The reddish pink solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator.

Yield 1.2g.

The orange brown dye has a m.p. 260-262°C. The ethanolic solution of the dye is light yellow in colour that turns into violet on adding a drop of an alkali.

The purity of the dye was tested by paper chromatography adopting technique

1A 1B

Paper used

Whatman No 1

Mobile phase

Butanol saturated with ammonia

Developing agent

1% aqueous caustic soda

Reference dye

Phenolphthalein

A 25-cm X 10 cm strip of Whatman filter paper was cut and a very dilute solution

was spotted with a microsyringe on a base line 4.0-cm from the bottom end. Similarly, a very dilute aqueous solution of the reference dye was also spotted 3.0 cm away from the first spot on the base line. The mobile phase was allowed to run for thirteen hours. The paper was then taken out, dried and sprayed with the developing agent. The developed chromatogram revealed only one spot for each of the two dyes. This was enough to confirm the homogeneity and purity of the dye.

Found R_f (Phenolphthalein): 0.92

R_f (5-chloro-2methylphenyl) phenol tetrachloro phthal-as-ein: 0.93

Reported R_f (Phenolphthalein) 0.91

Anal. For.: $C_{21}H_{11}Cl_5O_3$ (Mol. Wt. 488.55)

Calc. : C, 51.59; H, 2.25; Cl, 36.34

Found : C, 51.51; H, 2.24; Cl, 36.31

3.5.2 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) CATECHOL

TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.5g of the acid and 1.2g of catechol in an oil bath at 110 °C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of 2-hydroxy-5-methylphenyl phenol phthal-as-ein described in subsection 3.1.1. Yield 1.6g.

The black crystalline dye having a m.p. 250 °C is soluble in acetone, ethanol, methanol and acetic acid. It yields a light brown colour in ethanol that turns to golden brown on adding a drop of an alkali.

Anal. For.: $C_{21}H_{11}Cl_5O_4$ (Mol. Wt. 504.5)

Calc. : C, 49.95; H, 2.18; Cl, 35.18

Found : C, 49.85; H, 2.17; Cl, 35.16

3.5.3 PREPARATION OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

It was prepared by the condensation of 4.0g of the acid and 2.5g of resorcinol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 140-160 °C for about four and half-hours. It was isolated and purified as described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein earlier in the chapter. Yield 4.2g. The lemon yellow dye having a m.p. 298 -300 °C is soluble in acetic acid, ethanol and methanol and chloroform. It dissolves in ethanol giving a pale cream colour with green fluorescence that becomes more intense on adding a drop of an alkali.

Anal. For.: $C_{21}H_{11}Cl_5O_4$ (Mol. Wt. 504.5)

Calc. : C, 49.95; H, 2.18; Cl, 35.18

Found : C, 49.90; H, 2.16; Cl, 35.15

3.5.4 PREPARATION OF (5-CHLORO-2-METHYLPHENYL)

HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180 °C for four hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 1.2g.

The black dye, decomposing above 300 °C is soluble in ethanol giving a golden brown colour that turns into yellowish brown on the addition of a drop of an alkali.

Anal. For.: $C_{21}H_{11}Cl_5O_4$ (Mol. Wt. 504.5)

Calc. : C, 49.95; H, 2.18; Cl, 35.18

Found : C, 49.90; H, 2.16; Cl, 35.17

3.5.5 PREPARATION OF (5-CHLORO-2-METHYLPHENYL)

PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The mixture of 1.6g of the acid and 1.1g of pyrogallol was condensed together in

presence of a few drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier. Yield 1.2g.

The black coloured dye having m.p. above 180°C. The ethanolic solution is brown in colour which on adding a drop of an alkali becomes blackish brown and violet in moderate and strong basic media respectively.

Anal. For. : $C_{21}H_{11}Cl_5O_5$ (Mol. Wt. 520.5)

Calc. : C, 48.41; H, 2.11; Cl, 34.10

Found : C, 48.39; H, 2.10; Cl, 34.08

3.5.6 PREPARATION OF (5-CHLORO-2-METHYLPHENYL)

PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.6g of the acid and 1.2g of phluroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 190-200 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.3 early in this chapter. Yield 1.4g.

The grey coloured dye (decomposes >300 °C) yields a grey coloured solution in ethanol that turns pale cream on adding a drop of an alkali. It is soluble in acetone, ethanol, methanol and in acetic acid.

Anal. For. : $C_{21}H_{11}Cl_5O_5$ (Mol. Wt. 520.5)

Calc. : C, 48.41; H, 2.11; Cl, 34.10

Found : C, 48.40; H, 2.10; Cl, 34.07

3.5.7 ACETYLATION OF (5-CHLORO-2-METHYLPHENYL)

RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIACETYL RESORCINOL

TETRACHLORO PHTHAL-AS-EIN]

1.0g of the 5-chloro-2methylphenyl resorcinol tetrachloro phthal-as-ein dye, 3.0g

of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The acetylation, isolation and purification of the dye was carried out in exactly the same manner as in the case of (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter. Yield 0.62g.

The buff coloured microcrystalline diacetyl derivative (m.p. 180-182 °C) is soluble in benzene, ether, chloroform and acetic acid.

Anal. For.: $C_{25}H_{15}Cl_5O_6$ or $C_{21}H_9Cl_5O_4(OC.CH_3)_2$ (Mol. Wt. 588.5)

Calc. : C, 58.98; H, 2.55; Cl, 30.16 acetyl, 14.61

Found : C, 58.92; H, 2.53; Cl, 30.14 acetyl, 14.58

3.5.8 BROMINATION OF (5-CHLORO-2-METHYLPHENYL) RESORCINOL

TETRACHLORO PHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIBROMO RESORCINOL

TETRACHLORO PHTHAL-AS-EIN]

The 1.0-g of the dye (5-chloro-2-methylphenyl) resorcinol tetrachloro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A grey coloured substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 80 °C in an oven and then in a vacuum dessicator. Yield 0.86g.

The brownish cream tinged dye having m.p. 160-162 °C is soluble in benzene, methanol, acetone, and acetic acid and in chloroform.

Anal. For.: $C_{21}H_9Br_2Cl_5O_4$ (Mol. Wt. 662.5)

Calc. : Br, 24.15

Found : Br, 24.13

3.5.9 CAUSTIC POTASH TREATMENT OF (5-CHLORO-2-METHYLPHENYL)

RESORCINOL PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four and half hours till the dark colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark red residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II), which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. The compound, m. p. 180 °C (dec.), gives positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(5'-chloro-2'-methylbenzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

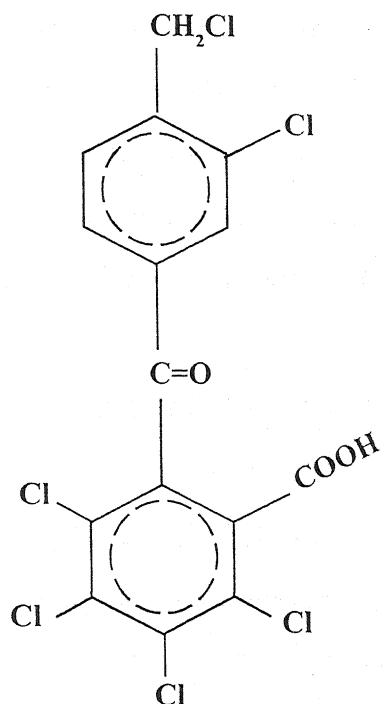
Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart B.

B.3

3.6 DYES DERIVED FROM 2-(3'-CHLORO-4'-CHLOROMETHYLBENZOYL)

TETRACHLORO BENZOIC ACID:



2-(3'-chloro-4'-chloromethylbenzoyl)tetrachlorobenzoic acid

Figure 3.11

3.6A PREPARATION OF 2-(3'-CHLORO-4'-CHLOROMETHYLBENZOYL)

TETRACHLORO BENZOIC ACID:

The acid²⁻⁶ was prepared by carrying out Friedel Crafts reaction between 2-chlorobenzyl chloride and tetrachloro phthalic anhydride and anhydrous AlCl_3 .

Starting with 2-chlorobenzylchloride(AR, dry 100ml),along with tetrachloro phthalic anhydride(28.5g,0.1mole) and anhydrous aluminium chloride (27.0g, about 0.2 moles) used as a catalyst, the acid was prepared following the procedure outlined in subsection 3.3A for the preparation of 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid.

The acid was isolated as dirty white crystals which had a melting point of 253-255°C (dec.). The crystalline solid was found to be soluble in acetone, chloroform and methanol. Yield 25.5 g.

Anal. For.: $\text{C}_{15}\text{H}_6\text{Cl}_6\text{O}_3$ (Mol. Wt. = 447)

Calc. : C, 40.27; H, 1.34; Cl, 47.65

Found : C, 40.24; H, 1.33; Cl, 47.60

3.6B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 120-130 °C in the same way as done for 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid described in subsection 3.3B in the beginning of the chapter. It was crystallised from acetone in the form of a brown solid, decomposing at 143-145 °C. It is soluble in ethanol, benzene, chloroform and acetic acid. Yield 0.60 g.

Anal. For.: $C_{17}H_8Cl_6O_4$ or $C_{15}H_5Cl_6O_3(OC.CH_3)$ (Mol. Wt. = 489)

Calc. : C, 41.72; H, 1.64; Cl, 43.56 acetyl. 8.79

Found : C, 41.70; H, 1.63; Cl, 43.53 acetyl. 8.76

The dyes prepared from the acid may be represented by the following structures:

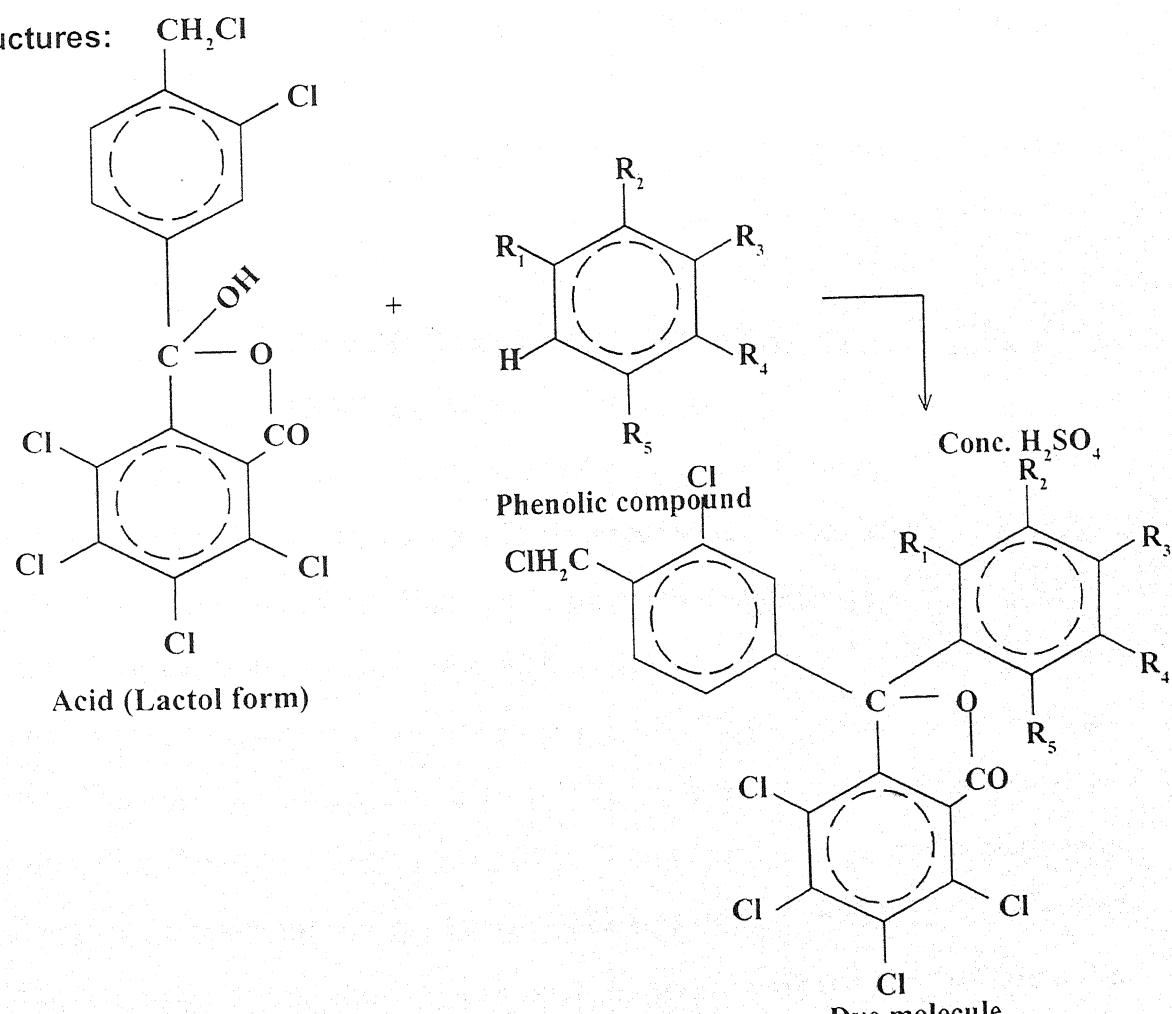
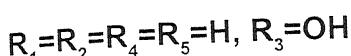


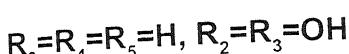
Figure 3.12

DYES:

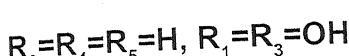
3.6.1 (3-chloro-4-chloromethylphenyl) phenol tetrachloro phthal-as-ein:



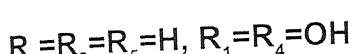
3.6.2 (3-chloro-4-chloromethylphenyl) catechol tetrachloro phthal-as-ein:



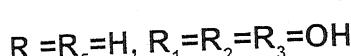
3.6.3 (3-chloro-4-chloromethylphenyl) resorcinol tetrachloro phthal-as-ein:



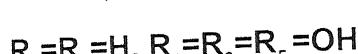
3.6.4 (3-chloro-4-chloromethylphenyl) hydroquinone tetrachloro phthal-as-ein:



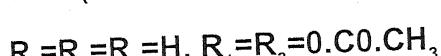
3.6.5 (3-chloro-4-chloromethylphenyl) pyrogallol tetrachloro phthal-as-ein:



3.6.6 (3-chloro-4-chloromethylphenyl) phloroglucinol tetrachloro phthal-as-ein:

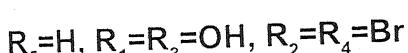


3.6.7 (3-chloro-4-chloromethylphenyl) diacetyl resorcinol tetrachloro phthal-as-ein:



3.6.8 (3-chloro-4-chloromethylphenyl) dibromo resorcinol tetrachloro phthal-as-

ein:



3.6.1 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL) PHENOL TETRACHLORO PHTHAL-AS-EIN:

A homogenized intimate mixture of 2.0 g of the acid and 1.5 g of phenol was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175 °C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The reddish pink solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit

and dried in vacuum in a dessicator. Yield 1.40g.

The pinkish white dye has a m.p. 240-242 °C. It is soluble in ethanol, acetone, ether and acetic acid. The ethanolic solution of the dye is light yellow in colour that turns into rose red colour on adding a drop of an alkali.

Anal. For.: $C_{21}H_{10}Cl_6O_3$ (Mol. Wt. 523)

Calc. : C, 48.18; H, 1.91; Cl, 40.73

Found : C, 48.15; H, 1.90; Cl, 40.71

3.6.2 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

CATECHOL TETRACHLORO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.0g each of the acid and catechol in an oil bath at 110 °C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of (2-hydroxy-5-methylphenyl) phenol phthal-as-ein described in subsection 3.1.1. Yield 1.6g.

The black crystalline dye having a m.p. 260 °C is soluble in ethanol to yield a light brown colour in ethanol that turns to dark brown on adding a drop of an alkali.

Anal. For.: $C_{21}H_{10}Cl_6O_4$ (Mol. Wt. 539)

Calc. : C, 46.75; H, 1.86; Cl, 39.52

Found : C, 46.73; H, 1.85; Cl, 39.51

3.6.3 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

It was prepared by the condensation of 4.50g of the acid and 2.5g of resorcinol (excess than the molecular proportion) on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 150-170 °C for about four and half-hours. It was isolated and purified as described for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein earlier in the chapter. Yield 3.0g.

The golden yellow crystalline dye having a m.p. 306-308 °C is soluble in acetic acid, ethanol and ether. It dissolves in ethanol giving a deep orange colour with green fluorescence with an alkali and pink colour with green fluorescence with alcoholic caustic potash solution.

Anal. For.: $C_{21}H_{10}Cl_6O_4$ (Mol. Wt. 539)

Calc. : C, 46.75; H, 1.86; Cl, 39.52

Found : C, 46.72; H, 1.85; Cl, 39.50

3.6.4 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

HYDROQUINONE TETRACHLORO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180 °C for three hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 1.2g.

The blackish brown dye, having m.p. above 360 °C is soluble in ethanol giving a leaf brown colour that turns into brown on the addition of 2% caustic soda solution.

Anal. For.: $C_{21}H_{10}Cl_6O_4$ (Mol. Wt. 539)

Calc. : C, 46.75; H, 1.86; Cl, 39.52

Found : C, 46.72; H, 1.85; Cl, 39.50

3.6.5 PREPARATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

PYROGALLOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and homogenised mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 135-145 °C for about three hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described earlier. Yield 0.70g.

The blackish brown coloured dye having m.p. above 360 °C gives an ethanolic solution leaf brown in colour which on adding a drop of an alkali becomes violet.

The colour remains violet in moderate and strong basic media respectively.

Anal. For. : $C_{21}H_{10}Cl_6O_5$ (Mol. Wt. 555)

Calc. : C, 45.41; H, 1.80; Cl, 31.98

Found : C, 45.38; H, 1.79; Cl, 31.96

3.6.6 PREPARATION OF (3 -CHLORO-4 -CHLOROMETHYLPHENYL) PHLOROGLUCINOL TETRACHLORO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.0g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 200-220 °C for about three hours. The isolation and purification of the dye was performed in the same way as that described for (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described in subsection 3.1.3 early in this chapter. Yield 0.80g.

The blackish brown coloured dye m.p. 310 °C (dec.) yields a golden brown coloured solution in ethanol that turns dark red on adding a drop of an alkali.

Anal. For. : $C_{21}H_{10}Cl_6O_5$ (Mol. Wt. 555)

Calc. : C, 45.41; H, 1.80; Cl, 38.38

Found : C, 45.40; H, 1.79; Cl, 38.36

3.6.7 ACETYLATION OF (3 -CHLORO-4 -CHLOROMETHYLPHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

[(3 -CHLORO-4 -CHLOROMETHYLPHENYL) DIACETYL RESORCINOL TETRACHLORO PHTHAL-AS-EIN]

1.0g of the (3-chloro-4-chloromethylphenyl) resorcinol tetrachloro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The acetylation, isolation and purification of acetylated product was carried out in exactly the same manner as in the case of (2-hydroxy-5-methylphenyl) resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter.

Yield 0.70g.

The buff coloured diacetyl derivative (m.p. 167-169 °C) is soluble in benzene, carbon

tetrachloride and chloroform.

Anal. For. : $C_{25}H_{14}Cl_6O_6$ or $C_{21}H_8Cl_6O_4$ ($OC.CH_3)_2$ (Mol. Wt. 623)

Calc. : C, 48.15; H, 2.25; Cl, 34.19 acetyl, 13.80

Found : C, 48.12; H, 2.24; Cl, 34.17 acetyl, 13.78

3.6.8 BROMINATION OF (3-CHLORO-4-CHLOROMETHYLPHENYL)

RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

[(3-CHLORO-4-CHLOROMETHYLPHENYL) DIBROMO RESORCINOL

TETRACHLORO PHTHAL-AS-EIN]

The 1.0-g of the dye 3-chloro-4-chloromethylphenyl resorcinol tetrachloro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10 ml of 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A blackish rose powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110 °C in an oven and then in a vacuum dessicator. Yield 1.10g.

The blackish rose coloured powdery dye having m.p. 325-327 °C is soluble in benzene, ethanol, and acetone.

Anal. For. : $C_{21}H_8Cl_6Br_2O_4$ (Mol. Wt. 697)

Calc. : Br, 22.96

Found : Br, 22.94

3.6.9 CAUSTIC POTASH TREATMENT OF (3-CHLORO-4-CHLOROMETHYLPHENYL) RESORCINOL TETRACHLORO PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a

few drops of water to turn them into a paste. 1.0g of the dye was then added to carry out the caustic potash treatment exactly in the same way as described in subsection 3.4.9 for (2-hydroxy-5-methylphenyl) resorcinol tetrachloro phthal-asein.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. It gives positive tests for carboxyl group and chlorine groups and was identified and confirmed as 2-(3'-chloro-4'-chloromethylbenzoyl) tetrachloro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.

Identification of residue III:

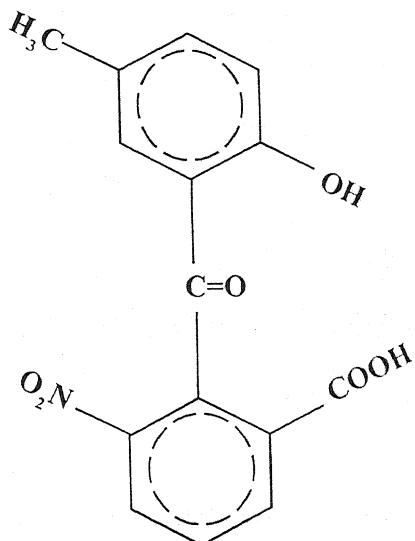
The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart C.

C.1

3.7 DYES DERIVED FROM 2-(2'HYDROXY-5'-METHYLBENZOYL) -3-

NITRO- BENZOIC ACID:



2-(2'-hydroxy-5'-methylbenzoyl)-3-nitrobenzoic acid

Figure 3.13

3.7A PREPARATION OF 2-(2'HYDROXY-5'-METHYLBENZOYL) -3-NITRO-BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between p-cresol (dry AR, 100 ml) and m-nitrophthalic anhydride (20g, about 0.1 mole) and anhydrous AlCl_3 (27.0g, about 0.2 moles) was used as a catalyst. The acid was isolated and purified exactly in the same manner as employed for 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid as reported in subsection 3.1A. Yield 20g

The acid was recrystallised from acetone as brown crystals. It had a melting point of 162-164°C. It was found to be soluble in acetone, ethanol and methanol.

Anal. For.: $\text{C}_{15}\text{H}_{11}\text{NO}_6$ (Mol. Wt. = 301)

Calc. : C, 59.80; H, 3.65; N, 4.65

Found : C, 59.76; H, 3.64; N, 4.63

3.7B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0g of the acid 3.5 g of fused sodium acetate was refluxed with 15 ml of freshly

distilled acetic anhydride at 120-130 °C for about four hours. The whole procedure was akin to the one outlined in subsection 3.1B for the acetylation of 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid.

The acetyl derivative was crystallised from acetone in the form of a brownish black solid that was treated with animal charcoal and finally recrystallised from aqueous ethanol in presence of a drop of acetic acid. Yield 0.80g.

It is a brown coloured solid, m.p. 135-137 °C. It is soluble in ethanol, methanol, chloroform and acetic acid.

Anal. For. : $C_{19}H_{15}NO_8$ or $C_{15}H_9NO_6(OC_2H_5)_2$ (Mol. Wt. = 385)

Calc. : C, 59.22; H, 3.90; N, 3.64 acetyl. 22.34

Found : C, 59.14; H, 3.86; N, 3.61 acetyl. 22.26

The dyes prepared from the acid may be represented by the following structures:

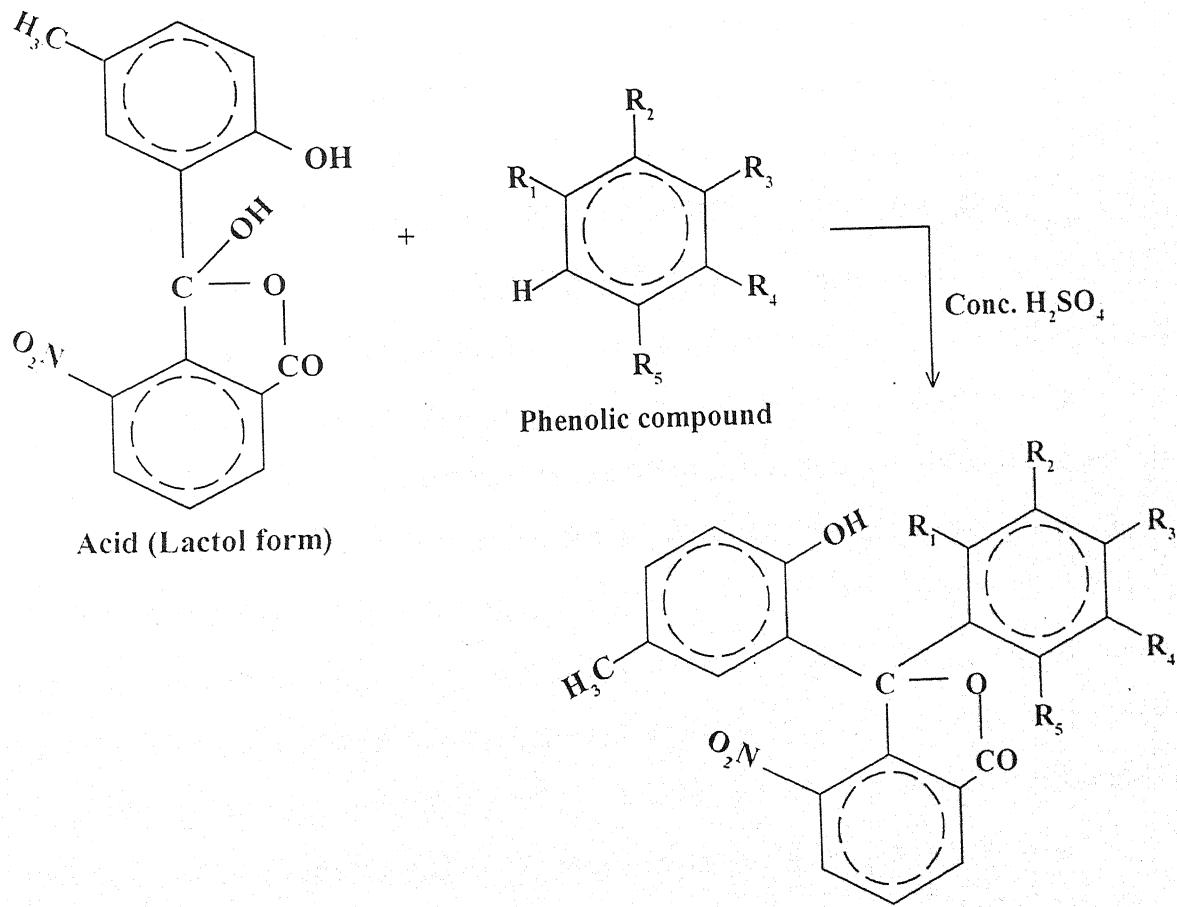
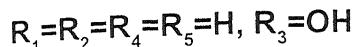


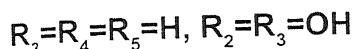
Figure 3.14

DYES:

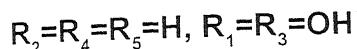
3.7.1 2-hydroxy-5-methylphenyl phenol nitro phthal-as-ein:



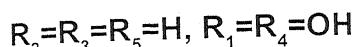
3.7.2 2-hydroxy-5-methylphenyl catechol nitro phthal-as-ein:



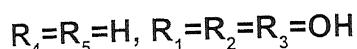
3.7.3 2-hydroxy-5-methylphenyl resorcinol nitro phthal-as-ein:



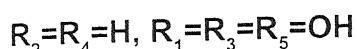
3.7.4 2-hydroxy-5-methylphenyl hydroquinone nitro phthal-as-ein:



3.7.5 2-hydroxy-5-methylphenyl pyrogallol nitro phthal-as-ein:



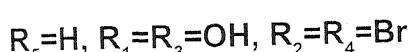
3.7.6 2-hydroxy-5-methylphenyl phloroglucinol nitro phthal-as-ein:



3.7.7 2-acetoxy-5-methylphenyl diacetyl resorcinol nitro phthal-as-ein:



3.7.8 3-bromo-2-hydroxy-5-methylphenyl dibromo resorcinol nitro phthal-as-ein:



3.7.1 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL PHENOL NITRO

PHTHAL-AS-EIN:

A homogenized intimate mixture of 1.5 g of the acid and 1.0 g of phenol was condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175°C for about four hours. The isolation of the dye was carried out exactly in the same manner as for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein outlined in subsection 3.1.1. Yield 1.2g.

The brown dye that is microcrystalline in nature has a m.p. > 360°C. The ethanolic solution of the dye is light brown in colour that turns into pink on adding a drop of an alkali. In strong basic medium, it gives light pink colour. The dye is soluble in methanol, ethanol and acetone.

Anal. For.: $C_{21}H_{15}NO_6$

(Mol. Wt. 377)

Calc. : C, 66.84; H, 3.98; N, 3.71

Found : C, 66.75; H, 3.96; N, 3.69

3.7.2 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL CATECHOL

NITRO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.5g of the acid and 1.0g of catechol as done in a manner similar to that in the case of 2-hydroxy-5-methylphenyl phenol phthal-as-ein described in subsection 3.1.1. Yield 1.2g.

The brownish black coloured dye has a m.p. $>360^{\circ}\text{C}$. It yields a golden brown colour in ethanol that turns to brown on adding a drop of an alkali.

Anal. For. : $\text{C}_{21}\text{H}_{15}\text{NO}_7$ (Mol. Wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56

Found : C, 64.01; H, 3.78; N, 3.51

3.7.3 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL NITRO PHTHAL-AS-EIN:

It was prepared by the condensation of 5.0g of the acid and 3.0g of resorcinol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at $140-160^{\circ}\text{C}$ for about four and half-hours. It was isolated and purified as described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein earlier in the chapter. Yield 4.0g. The greenish brown dye having a m.p. $301-303^{\circ}\text{C}$ is soluble in acetic acid, acetone, ethanol and methanol. It dissolves in ethanol giving a light yellow colour that turns into brownish red with green fluorescence on adding a drop of an alkali.

Anal. For. : $\text{C}_{21}\text{H}_{15}\text{NO}_7$ (Mol. Wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56

Found : C, 64.03; H, 3.79; N, 3.52

3.7.4 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL HYDROQUINONE NITRO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at $160-180^{\circ}\text{C}$ for three hours in presence of a few drops of concentrated sulphuric acid. The isolation and

purification of the dye was carried out in a manner similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 1.2g.

The black dye, decomposing above 262 °C is soluble in ethanol giving light brown colour that turns into brown on the addition of a drop of an alkali.

Anal. For. : $C_{21}H_{15}NO_7$ (Mol. Wt. 393)

Calc. : C, 64.12; H, 3.82; N, 3.56

Found : C, 63.97; H, 3.80; N, 3.53

3.7.5 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL PYROGALLOL

NITRO PHTHAL-AS-EIN:

The mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier. Yield 1.3g.

The brownish black coloured dye having m.p. 360 °C is soluble in methanol, acetone, alcohol and acetic acid. The ethanolic solution is light brown in colour that on adding a drop of an alkali darkens considerably.

Anal. For. : $C_{21}H_{15}NO_8$ (Mol. Wt. 409)

Calc. : C, 61.61; H, 3.67; N, 3.42

Found : C, 61.53; H, 3.63; N, 3.40

3.7.6 PREPARATION OF 2-HYDROXY-5-METHYLPHENYL

PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.0g of phluroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 180-200 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for the other dyes. Yield 1.2g.

The dark red coloured dye (m.p. > 360 °C) yields a wine red coloured solution in ethanol that turns orange red on adding a drop of an alkali. It is soluble in benzene, acetone, and ethanol and in acetic acid.

Anal. For.: $C_{21}H_{15}NO_8$ (Mol. Wt. 409)

Calc. : C, 61.61; H, 3.67; N, 3.42

Found : C, 61.52; H, 3.64; N, 3.39

3.7.7 ACETYLATION OF 2-HYDROXY-5-METHYLPHENYL

RESORCINOL NITRO PHTHAL-AS-EIN:

[(2-ACETOXY-5-METHYLPHENYL) DIACETYL RESORCINOL NITRO

PHTHAL-AS-EIN]

1.0g of the dye 2-hydroxy-5-methylphenyl resorcinol nitro phthal-as-ein's, acetylation, isolation and purification was carried out in exactly the same manner as in the case of 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter. Yield 0.80g.

The light yellow coloured triacetyl derivative (m.p. 242 °C) is soluble in acetone alcohol and acetic acid.

Anal. For.: $C_{27}H_{21}NO_{10}$ or $C_{21}H_{12}NO_7(OC.CH_3)_3$ (Mol. Wt. 519)

Calc. : C, 62.43; H, 4.05; N, 2.70 acetyl, 24.86

Found : C, 62.33; H, 4.01; N, 2.70 acetyl, 24.82

3.7.8 BROMINATION OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

[(3-BROMO-2-HYDROXY-5-METHYLPHENYL) DIBROMO RESORCINOL

NITRO PHTHAL-AS-EIN]

The 1.0-g of the dye 2-hydroxy-5-methylphenyl resorcinol nitro phthal-as-ein was brominated, isolated and purified as described in subsection 3.1.8 for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein dye and dried at 80 °C in an oven and then in a vacuum dessicator. Yield 0.80g.

The brownish dye having m.p. 174 °C is soluble in tinged ether, chloroform and

acetic acid.

Anal. For.: $C_{21}H_{12}NBr_3O_7$ (Mol. Wt. 630)

Calc. : Br, 38.10

Found : Br, 38.02

3.7.9 CAUSTIC POTASH TREATMENT OF 2-HYDROXY-5-METHYLPHENYL RESORCINOL NITRO PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were treated in a manner as outlined in sub section 3.1.9 for the caustic potash fusion of 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein. Consequently three residues I, II and III were obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. It gave positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(2'-hydroxy-5'-methylbenzoyl)-3-nitro-benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

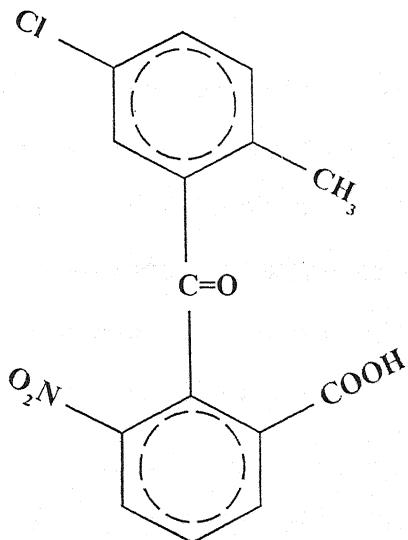
Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart A.

C.2

3.8 DYES DERIVED FROM 2-(5'CHLORO-2'-METHYLBENZOYL) -3-NITRO

- BENZOIC ACID:



2-(5'-chloro-2'-methylbenzoyl)-3-nitrobenzoic acid

Figure 3.15

3.8A PREPARATION OF 2-(5'-CHLORO-2'-METHYLBENZOYL) -3-NITRO -

BENZOIC ACID:

The acid⁹⁻¹³ was prepared by carrying out Friedel Crafts reaction between 4-chlorotoluene (dry AR, 85 ml) and 3-nitro phthalic anhydride (20.0 g, about 0.1 mole) and anhydrous AlCl₃ (27.0 g, about 0.2 moles) was used as a catalyst. Yield 20.0 g.

The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap. The reaction was carried out below 25°C by adding AlCl₃ in portions. When the vigorous reaction subsided, the mixture was heated on a boiling water bath until evaporation of HCl ceased.

The heavy dark brown coloured complex was precipitated by the addition of concentrated hydrochloric acid in 250 ml-ice cold water. It was filtered off, washed

well with cold water, dried and recrystallised from acetone/methanol. It has a melting point of 185-187°C. The light pink crystalline solid was found to be soluble in acetone and methanol.

Anal. For.: $C_{15}H_{10}NCIO_5$ (mol. Wt. = 319.5)

Calc. : C, 56.34; H, 3.13; N; 4.38, Cl, 11.11

Found : C, 56.31; H, 3.12; N; 4.36, Cl, 11.10

3.8B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 130°C for about four hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a brown coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was crystallised from acetone in the form of a light brown solid, with a m.p. 109-110 °C. It is soluble in acetone, chloroform and acetic acid. Yield 0.75 g.

Anal. For.: $C_{17}H_{12}NCIO_6$ or $C_{15}H_9NCIO_5(OC.CH_3)$ (Mol. Wt. = 361.5)

Calc. : C, 56.43; H, 3.32; N, 3.87; Cl, 9.82; acetyl., 11.89

Found : C, 56.40; H, 3.31; N, 3.85; Cl, 9.80; acetyl. 11.87

The dyes prepared from the acid may be represented by the following structures:

PLEASE TURN OVER

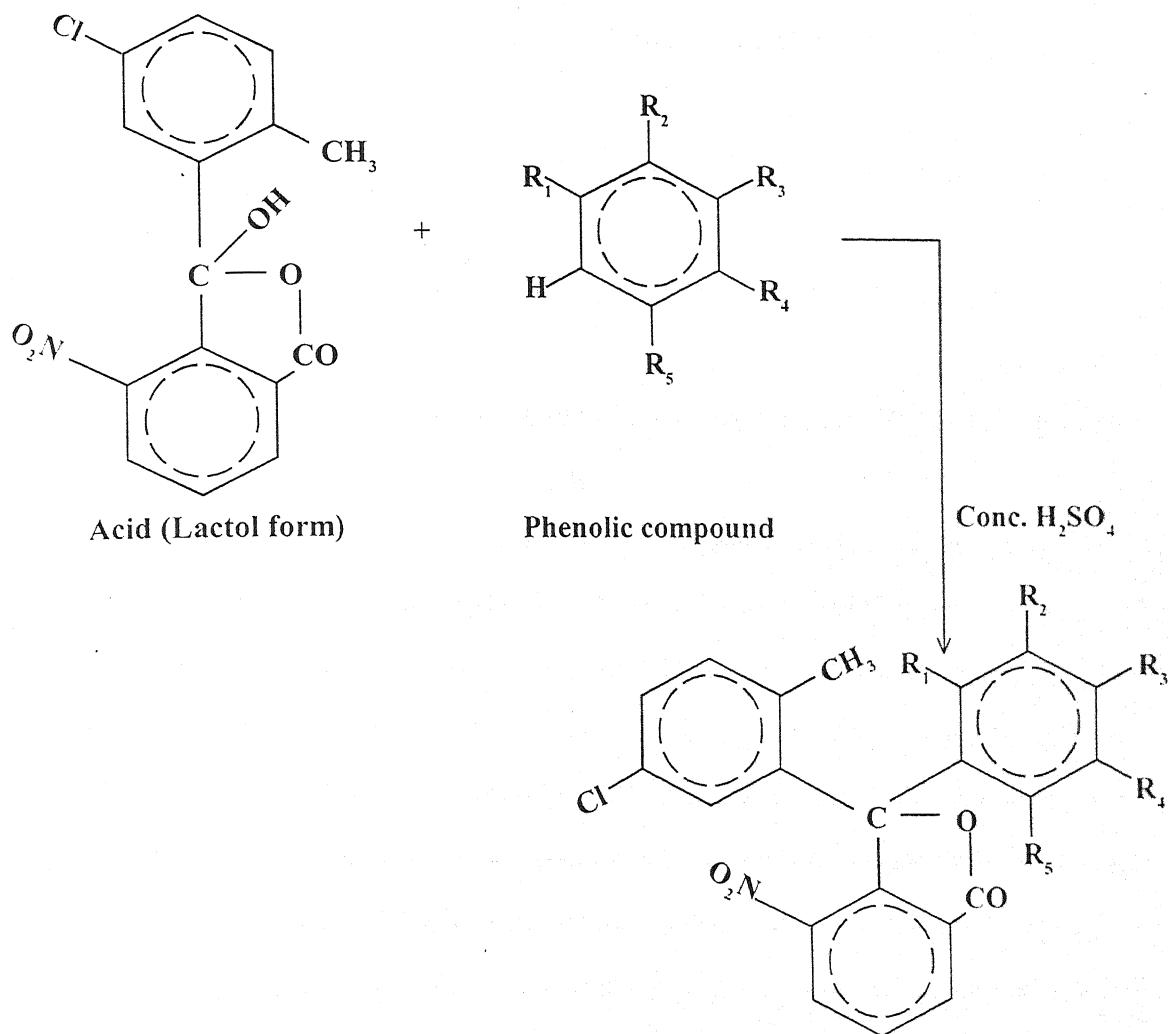
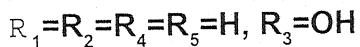


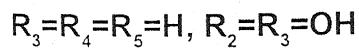
Figure 3.16 Dye molecule

DYES:

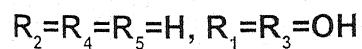
3.8.1 5-chloro-2methylphenyl phenol nitro phthal-as-ein:



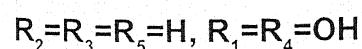
3.8.2 5-chloro-2methylphenyl catechol nitro phthal-as-ein:



3.8.3 5-chloro-2methylphenyl resorcinol nitro phthal-as-ein:



3.8.4.5-chloro-2methylphenyl hydroquinone nitro phthal-as-ein:



3.8.5 5-chloro-2methylphenyl pyrogallol nitro phthal-as-ein:

$$R_4 = R_5 = H, R_1 = R_2 = R_3 = OH$$

3.5.6 5-chloro-2methylphenyl phloroglucinol nitro phthal-*as-ein*:

$$R_2 = R_4 = H, R_1 = R_3 = R_5 = OH$$

3.8.7 5-chloro-2-methylphenyl diacetyl resorcinol nitro phthal-*as-ein*:

$R_2 = R_4 = R_5 = H, R_1 = R_3 = O.COO.CH_3$

3.8.8 5-chloro-2-methylphenyl dibromo resorcinol nitro phthal-*as-ein*:

$R_5 = H, R_1 = R_2 = OH, R_3 = R_4 = Br$

3.8.1 PREPARATION OF 5-chloro-2-methylphenyl phenol NITRO phthal-ase

The dye was prepared starting from a homogenized intimate mixture of 1.5 g of the acid and 1.0 g of phenol (slight excess than molecular proportion) in a hard boiling tube, heating it at 120 °C for some time to make it homogeneous and then condensing in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-170 °C for about six hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The dark solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the blackish brown coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 1.3g.

The blackish brown dye has a m.p. 300°C (dec.). The ethanolic solution of the dye is brown in colour that turns into reddish violet on adding a drop of an alkali.

The purity of the dye was tested by paper chromatography adopting technique 1A.1B.

Mobile phase Butanol saturated with ammonia

Developing agent 1% aqueous caustic soda

Reference dye Phenolphthalein

Found R_f (Phenolphthalein): 0.93

R_f 5-chloro-2methylphenyl phenol nitro phthal-as-ein:	0.95
Reported R_f (Phenolphthalein)	0.92

Anal. For.: $C_{21}H_{14}NCIO_5$ (Mol. Wt. 395.5)

Calc. : C, 63.72; H, 3.54; N, 3.54; Cl, 8.98

Found : C, 63.70; H, 3.53; N, 3.52; Cl, 8.96

3.8.2 PREPARATION OF 5-CHLORO-2-METHYLPHENYL CATECHOL

NITRO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.2g of the acid and 1.0g of catechol in an oil bath at 120-130°C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of 2-hydroxy-5-methylphenyl phenol phthal-as-ein described in subsection 3.1.1. Yield 1.5g. m.p. >360°C.

The black dye yields a brown colour in ethanol that turns to brownish black on adding a drop of an alkali.

Anal. For.: $C_{21}H_{14}NCIO_6$ (Mol. Wt. 411.5)

Calc. : C, 61.24; H, 3.40; N, 3.40; Cl, 8.63

Found : C, 61.22; H, 3.39; N, 3.38; Cl, 8.60

3.8.3 PREPARATION OF 5-CHLORO-2-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

It was prepared by the condensation of 5.0g of the acid and 3.0g of resorcinol on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 140-160°C for about four and half-hours. It was isolated and purified as described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein earlier in the chapter. Yield 4.2g The greenish brown dye having a m.p. 312°C (dec.) dissolves in ethanol giving a lemon yellow colour which becomes more intense with green fluorescence on adding a drop of an alkali. It is soluble in ethanol, methanol and acetic acid.

Anal. For.: $C_{21}H_{14}NCIO_6$ (Mol. Wt. 411.5)

Calc. : C, 61.24; H, 3.40; N, 3.40; Cl, 8.63

Found : C, 61.22; H, 3.39; N, 3.38; Cl, 8.61

3.8.4 PREPARATION OF 5-CHLORO-2-METHYLPHENYL HYDROQUINONE

NITRO PHTHAL-AS-EIN:

1.2g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180 °C for four hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 0.85g.

The black dye, decomposing above 234 °C is soluble in ethanol giving a light brown colour that turns into dark brown on the addition of a drop of an alkali. The dye is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For.: $C_{21}H_{14}NCIO_6$ (Mol. Wt. 411.5)

Calc. : C, 61.24; H, 3.40; N, 3.40; Cl, 8.63

Found : C, 61.21; H, 3.39; N, 3.37; Cl, 8.61

3.8.5 PREPARATION OF 5-CHLORO-2-METHYLPHENYL PYROGALLOL

NITRO PHTHAL-AS-EIN:

The mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about four hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier. Yield 1.2g.

The black coloured amorphous dye having m.p. above 360 °C has an ethanolic solution which is light brown in colour on adding a drop of an alkali becomes brown. It is soluble in acetone, ethanol, methanol and acetic acid.

Anal. For.: $C_{21}H_{14}NCIO_7$ (Mol. Wt. 427.5)

Calc. : C, 58.95; H, 3.27; N, 3.27; Cl, 8.30

Found : C, 58.92; H, 3.26; N, 3.25; Cl, 8.27

3.8.6 PREPARATION OF 5-CHLORO-2-METHYLPHENYL

PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.2g of the acid and 1.0g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 190-200 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.3 early in this chapter. Yield 0.90g.

The brownish red dye (decomposing at 320 °C) yields an orange red colour solution in ethanol that turns deep orange red on adding a drop of an alkali. It is soluble in benzene, acetone, methanol and in acetic acid.

Anal. For.: $C_{21}H_{14}NCIO_7$ (Mol. Wt. 427.5)

Calc. : C, 58.95; H, 3.27; N, 3.27; Cl, 8.30

Found : C, 58.92; H, 3.26; N, 3.25; Cl, 8.28

3.8.7 ACETYLATION OF 5-CHLORO-2-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIACETYL RESORCINOL NITRO

PHTHAL -AS-EIN]

1.0g of the 5-chloro-2methylphenyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The acetylation, isolation and purification of the dye and the acetylated product was carried out in exactly the same manner as in the case of 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter. Yield 0.62g.

The pale cream coloured diacetyl derivative (m.p. 280 °C) is soluble in acetone,

methanol and acetic acid.

Anal. For.: $C_{25}H_{18}NCIO_8$ or $C_{21}H_{12}NCIO_6(OC.CH_3)_2$ (Mol. Wt. 495.5)

Calc. : C, 60.54; H, 3.63; N, 2.83; Cl, 7.16 acetyl, 17.36

Found : C, 60.52; H, 3.62; N, 2.81; Cl, 7.14 acetyl, 17.34

3.8.8 BROMINATION OF 5-CHLORO-2-METHYLPHENYL RESORCINOL

NITRO PHTHAL-AS-EIN:

[(5-CHLORO-2-METHYLPHENYL) DIBROMO RESORCINOL NITRO

PHTHAL-AS-EIN]

The 1.0-g of the dye 5-chloro-2-methylphenyl resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130°C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A dark brown coloured substance settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 80°C in an oven and then in a vacuum dessicator.

Yield 0.70g.

The dark brown microcrystalline dye having m.p. 182°C is soluble in ether, ethanol, methanol, and acetic acid and in chloroform.

Anal. For.: $C_{21}H_{12}NCIBr_2O_6$ (Mol. Wt. 569.5)

Calc. : Br, 28.09

Found : Br, 28.05

3.8.9 CAUSTIC POTASH TREATMENT OF 5-CHLORO-2-METHYLPHENYL RESORCINOL NITRO PHTHAL-AS-EIN:

5.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four and half hours till the dark colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark red residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II), which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. The compound, m. p. 180 °C (dec.), gives positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(5'-chloro-2'-methylbenzoyl) -3-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

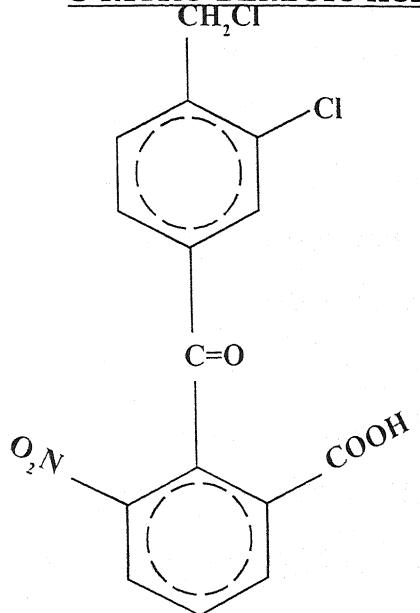
Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart B.

C.3

3.9 DYES DERIVED FROM 2-(3'-CHLORO-4'-CHLOROMETHYLBENZOYL)

3-NITRO BENZOIC ACID:



2-(3'-chloro-4'-chloromethylbenzoyl)-3-nitrobenzoic acid

Figure 3.17

3.9A PREPARATION OF 2-(3'-CHLORO-4'-CHLOROMETHYLBENZOYL) 3-NITRO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between o-chlorobenzyl chloride and m-nitro phthalic anhydride and anhydrous AlCl_3 . Starting with o-chlorobenzylchloride (AR, dry 100ml), along with m-nitro phthalic anhydride (20.0g, 0.1 mole) and anhydrous aluminum chloride (27.0g, about 0.2 moles) used as a catalyst, the acid was prepared following the procedure outlined in subsection 3.6A for the preparation of 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid.

The acid was isolated as shining white crystals, which had a melting point of 190-192 °C. The crystalline solid was found to be soluble in rectified spirit and methanol. Yield 18.0 g.

Anal. For.: $C_{15}H_9NCl_2O_5$ (Mol. Wt. = 354)

Calc. : C, 50.85; H, 2.54; N, 3.95; Cl, 20.06

Found : C, 50.83; H, 2.53; N, 3.93; Cl, 20.03

3.9B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 130-140°C in the same way as done for 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid described in subsection 3.1B in the beginning of the chapter. It was crystallised from acetone in the form of a black crystalline solid, m.p. 244°C. It is slightly soluble in methanol but highly soluble in acetone. Yield 0.60 g.

Anal. For.: $C_{17}H_{11}NCl_2O_6$ or $C_{15}H_8NCl_2O_5$ ($OC.CH_3$) (Mol. Wt. = 396)

Calc. : C, 51.52; H, 2.78; N, 3.54; Cl, 17.93; acetyl. 10.86

Found : C, 51.50; H, 2.77; N, 3.52; Cl, 17.90; acetyl. 10.84

The dyes prepared from the acid may be represented by the following

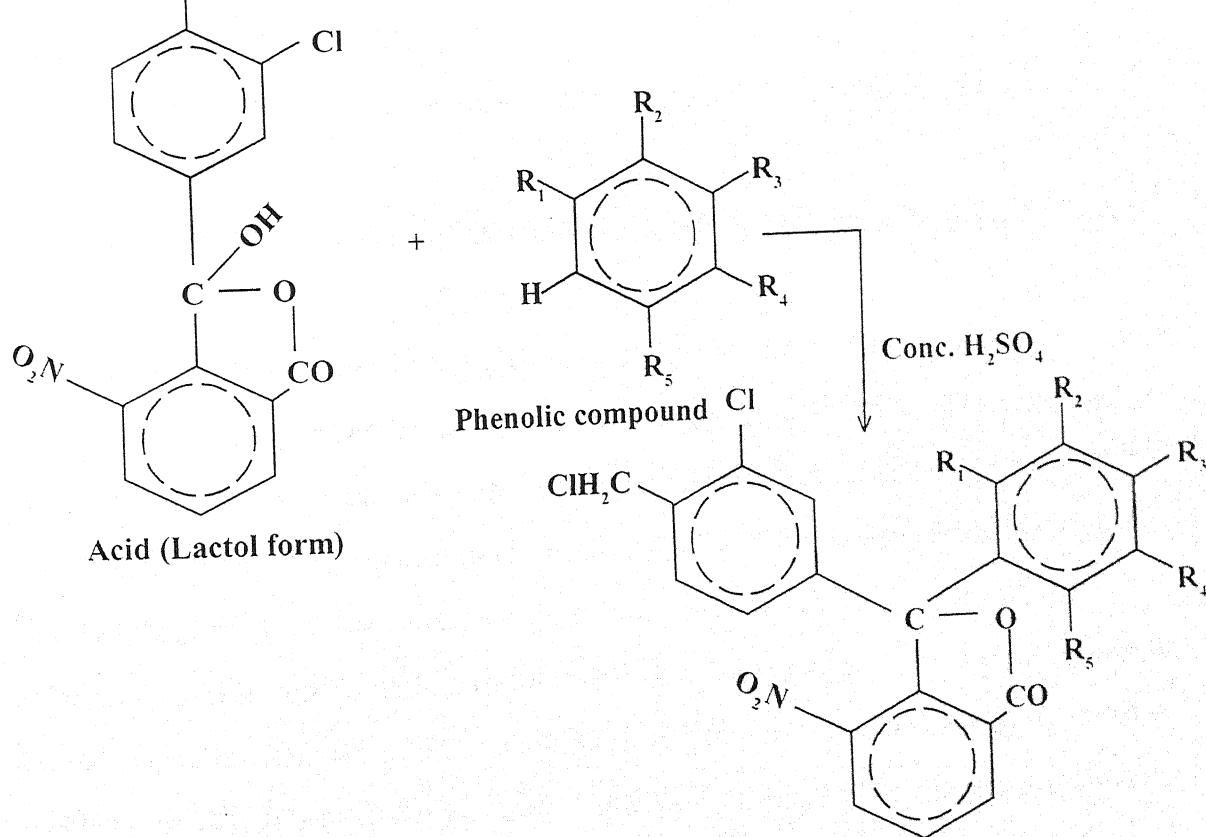


Figure 3.18

structures:

DYES:

3.9.1 3-chloro-4-chloromethylphenyl phenol nitro phthal-as-ein:

$R_1=R_2=R_4=R_5=H$, $R_3=OH$

3.9.2 3-chloro-4-chloromethylphenyl catechol nitro phthal-as-ein:

$R_3=R_4=R_5=H$, $R_2=R_3=OH$

3.9.3 3-chloro-4-chloromethylphenyl resorcinol nitro phthal-as-ein:

$R_2=R_4=R_5=H$, $R_1=R_3=OH$

3.9.4 3-chloro-4-chloromethylphenyl hydroquinone nitro phthal-as-ein:

$R_2=R_3=R_5=H$, $R_1=R_4=OH$

3.9.5 3-chloro-4-chloromethylphenyl pyrogallol nitro phthal-as-ein:

$R_4=R_5=H$, $R_1=R_2=R_3=OH$

3.9.6 3-chloro-4-chloromethylphenyl phloroglucinol nitro phthal-as-ein:

$R_2=R_4=H$, $R_1=R_3=R_5=OH$

3.9.7 3-chloro-4-chloromethylphenyl diacetyl resorcinol nitro phthal-as-ein:

$R_2=R_4=R_5=H$, $R_1=R_3=O.C0.CH_3$

3.9.8 3-chloro-4-chloromethylphenyl dibromo resorcinol nitro phthal-as-ein:

$R_5=H$, $R_1=R_3=OH$, $R_2=R_4=Br$

3.9.1 PREPARATION OF 3-CHLORO-4-CHLOROMETHYLPHENYL PHENOL

NITRO PHTHAL-AS-EIN:

An intimate mixture of 2.0 g of the acid and 1.5 g of phenol was heated in a hard boiling tube to make it homogeneous. It was then condensed in an oil bath in presence of 3-4 drops of concentrated sulphuric acid at 160-175°C for about four and half hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator.

Yield 1.20g.

The light pink dye has a m.p. 214-216 °C. The ethanolic solution of the dye is light brown in colour that turns into violet colour on adding a drop of an alkali.

The purity of the dye was tested as done in the case of other phenol dyes described in earlier pages.

Anal. For.: $C_{21}H_{13}NCl_2O_5$ (Mol. Wt. 430)

Calc. : C, 58.60; H, 3.02; N, 3.26; Cl, 16.51

Found : C, 58.58; H, 3.01; N, 3.25; Cl, 16.50

3.9.2 PREPARATION OF 3-CHLORO-4-CHLOROMETHYLPHENYL

CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.0g each of the acid and catechol in an oil bath at 115 °C to make it uniform and homogeneous. Then the intimate mixture was condensed for four and half hours in presence of a few drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of 2-hydroxy-5-methylphenyl phenol phthal-as-ein described in subsection 3.1.1. Yield 0.6g.

The black dye having a m.p. 314-316 °C is soluble in ethanol to yield a brown colour in ethanol that turns to reddish brown with alcoholic caustic soda solution.

Anal. For.: $C_{21}H_{13}NCl_2O_6$ (Mol. Wt. 446)

Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92

Found : C, 56.47; H, 2.90; N, 3.11; Cl, 15.90

3.9.3 PREPARATION OF 3-CHLORO-4-

CHLOROMETHYLPHENYLRESORCINOL NITRO PHTHAL-AS-EIN:

It was prepared by the condensation of 5.0g of the acid and 2.5g of resorcinol (a little excess than the molecular proportion) on an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 150-170 °C for about four and half-hours. It was isolated and purified as described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein earlier in the chapter. Yield 3.0g.

The golden yellow crystalline dye having a m.p. 225-227 °C. It dissolves in ethanol

giving a brown colour with an alkali and reddish brown colour with 2% caustic soda solution.

Anal. For.: $C_{21}H_{13}NCl_2O_6$ (Mol. Wt. 446)

Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92

Found : C, 56.47; H, 2.90; N, 3.12; Cl, 15.89

3.9.4 PREPARATION OF 3-CHLORO-4-CHLOROMETHYLPHENYL HYDROQUINONE NITRO PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 160-180 °C for three hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier in subsection 3.1.3 of the chapter. Yield 1.2g.

The blackish brown dye, having m.p. above 320-321 °C is soluble in ethanol giving a brown colour that turns into reddish brown on the addition of 2% caustic solution.

Anal. For.: $C_{21}H_{13}NCl_2O_6$ (Mol. Wt. 446)

Calc. : C, 56.50; H, 2.91; N, 3.14; Cl, 15.92

Found : C, 56.42; H, 2.90; N, 3.11; Cl, 15.90

3.9.5 PREPARATION OF 3-CHLORO-4-CHLOROMETHYLPHENYL PYROGALLOL NITRO PHTHAL-AS-EIN:

The intimate and homogenised mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of a few drops of concentrated sulphuric acid on an oil bath at 200-220 °C for about three hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described earlier. Yield 0.80g.

The black coloured dye having m.p. above 340-342 °C gives an ethanolic solution reddish brown in colour which on adding a drop of an alkali darkens in shade.

Anal. For.: $C_{21}H_{13}NCl_2O_7$

(Mol. Wt. 462)

Calc. : C, 54.55; H, 2.81; N, 3.03; Cl, 15.37

Found : C, 54.52; H, 2.80; N, 3.01; Cl, 15.35

3.9.6

PREPARATION OF 3 -CHLORO-4 -CHLOROMETHYLPHENYL PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.0g of the acid and 1.0g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 200-220 °C for about three hours. The isolation and purification of the dye was performed in the same way as that described for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein described in subsection 3.1.3 early in this chapter. Yield 0.65g.

The brown coloured dye m.p. 298-299 °C yields a wine red coloured solution in ethanol that turns dark red on adding a drop of an alkali. It gives wine red colour with alcoholic potash solution.

Anal. For.: $C_{21}H_{13}NCl_2O_7$

(Mol. Wt. 462)

Calc. : C, 54.55; H, 2.81; N, 3.03; Cl, 15.37

Found : C, 54.53; H, 2.80; N, 3.00; Cl, 15.34

3.9.7

ACETYLATION OF 3 -CHLORO-4 -CHLOROMETHYLPHENYL

RESORCINOL NITRO PHTHAL-AS-EIN:

[(3 -CHLORO-4 -CHLOROMETHYLPHENYL) DIACETYL

RESORCINOL NITRO PHTHAL-AS-EIN]

1.0g of the 3 -chloro-4 -chloromethylphenyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser and refluxed for about three hours. The isolation and purification of acetylated product was carried out in exactly the same manner as in the case of 2-hydroxy-5-methylphenyl

resorcinol phthal-as-ein described in subsection 3.1.7 in the first section of the chapter. Yield 0.70g.

The buff coloured diacetyl derivative (m.p. 264-266 °C) is soluble in acetone, methanol and chloroform.

Anal. For. : $C_{25}H_{17}NCl_2O_8$ or $C_{21}H_{11}NCl_2O_6$ ($OC.CH_3)_2$ (Mol. Wt. 530)

Calc. : C, 56.60; H, 3.21; N, 2.64; Cl, 13.40; acetyl, 16.23

Found : C, 56.52; H, 3.20; N, 2.63; Cl, 13.37; acetyl, 16.21

3.9.8 BROMINATION OF 3 -CHLORO-4 -CHLOROMETHYLPHENYL

RESORCINOL NITRO PHTHAL-AS-EIN:

[(3-CHLORO-4-CHLOROMETHYLPHENYL) DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

The 1.0-g of the dye 3-chloro-4-chloromethylphenyl resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10 ml of 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-130 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A blackish rose powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110 °C in an oven and then in a vacuum dessicator. Yield 0.90g.

The dark brown coloured crystalline dye having m.p. 175-176 °C is soluble in ethanol yielding a yellowish red colour that turns into orange with green fluorescence on adding a drop of an alkali. In strong alkaline medium, it exhibits deep red colour.

Anal. For.: $C_{21}H_{11}NBr_2Cl_2O_6$

(Mol. Wt. 604)

Calc. : Br, 26.49

Found : Br, 26.47

3.9.9 CAUSTIC POTASH TREATMENT OF 3-CHLORO-4-

CHLOROMETHYLPHENYL RESORCINOL NITRO PHTHAL-AS-EIN:

10.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to carry out the caustic potash treatment exactly in the same way as described in subsection 3.1.9 for 2-hydroxy-5-methylphenyl resorcinol phthal-as-ein.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from acetone. It gives positive tests for carboxyl group and chlorine groups and was identified and confirmed as 2-(3'-chloro-4'-chloromethylbenzoyl) nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.

Identification of residue III:

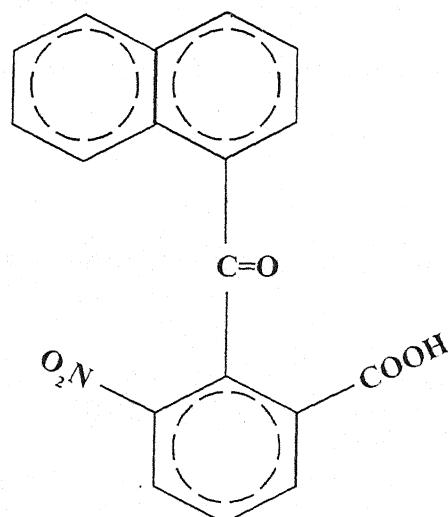
The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart C.

D.1

3.10 DYES DERIVED FROM 2-(α -NAPHTHOYL) -3-NITRO - BENZOIC

ACID:



2-(α -naphthoyl)-3-nitrobenzoic acid

Figure 3.19

3.10A PREPARATION OF 2-(α -NAPHTHOYL) -3-NITRO - BENZOIC ACID:

The acid¹ was prepared by carrying out Friedel Crafts reaction between naphthalene and 3-nitro phthalic anhydride in presence of anhydrous $AlCl_3$ (used as a catalyst. The acid was crystallised from aqueous ethanol. M.p.176-178°C. Fresh distilled and dried nitrobenzene (AR, 200ml) was used as solvent. Isolation of the acid was done in a manner exactly similar to that followed for the isolation of other γ -keto acids On fusion with caustic potash, the acid yielded α -naphthoic acid and (m.p.158-160°C) and 3-nitrobenzoic acid

Anal. For. : $C_{18}H_{11}NO_5$ (mol. Wt. = 321)

Calc. : C, 67.29; H, 3.43; N; 4.36

Found : C, 67.15; H, 3.41; N; 4.35

3.10B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of freshly distilled acetic anhydride at 130-140°C for about three and half hours. The hot contents were poured in a beaker containing ice cold water accompanied by constant stirring. The acetyl derivative settled down in the form of a dark brown

coloured solid mass. The coloured acetyl derivative was dissolved in acetone and treated with animal charcoal and filtered while hot. It was recrystallised from acetone in the form of a light brown solid. Yield 0.68g with a m.p. 268°C (dec.). It is soluble in acetone, chloroform, ethanol and acetic acid.

Anal. For.: $C_{20}H_{13}NO_6$ or $C_{18}H_{10}NO_5$ ($OC.CH_3$) (Mol. Wt. = 363)

Calc. : C, 66.12; H, 3.58; N, 3.86; acetyl., 11.85

Found : C, 66.02; H, 3.56; N, 3.84; acetyl., 11.78

The dyes prepared from the acid may be represented by the following structures:

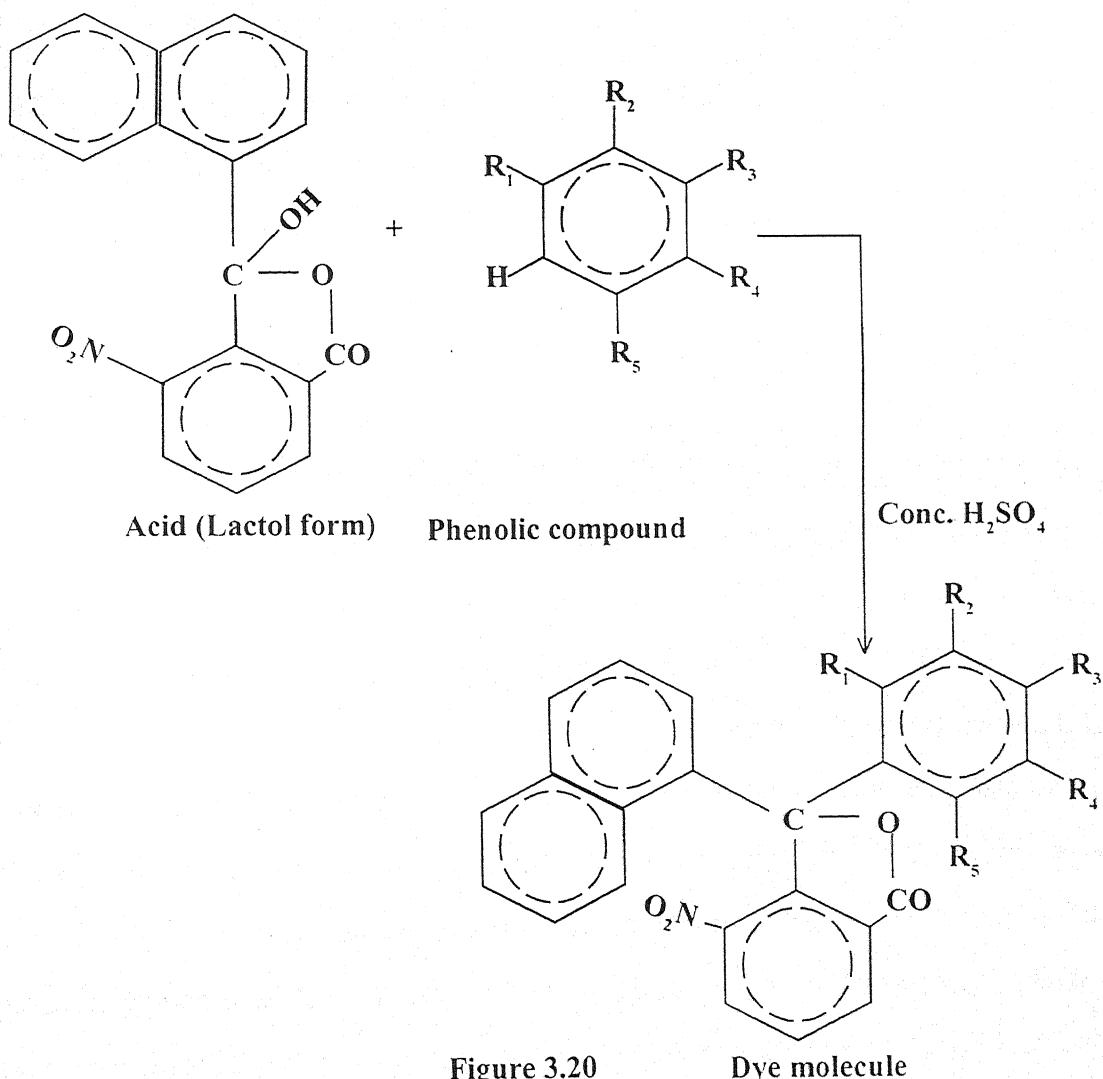
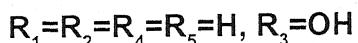


Figure 3.20

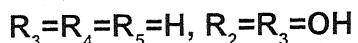
Dye molecule

DYES:

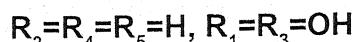
3.10.1 α -naphthyl phenol nitro phthal-as-ein:



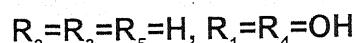
3.10.2 α -naphthyl catechol nitro phthal-as-ein:



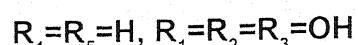
3.10.3 α -naphthyl resorcinol nitro phthal-as-ein:



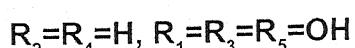
3.10.4 α -naphthyl hydroquinone nitro phthal-as-ein:



3.10.5 α -naphthyl pyrogallol nitro phthal-as-ein:



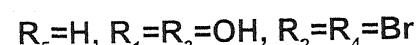
3.10.6 α -naphthyl phloroglucinol nitro phthal-as-ein:



3.8.7 α -naphthyl diacetyl resorcinol nitro phthal-as-ein:



3.10.8 α -naphthyl dibromo resorcinol nitro phthal-as-ein:



3.10.1 PREPARATION OF α -NAPHTHYL PHENOL NITRO PHTHAL-AS-EIN:

The dye was prepared starting from a homogenized intimate mixture of 2.50 g of the acid and 1.5 g of phenol (slight excess than molecular proportion) in a hard boiling tube, heating it at 120 °C for some time to make it homogeneous and then condensing in an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 160-180 °C for about six hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The brown solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the blackish brown coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 1.80g. m.p. 120 °C (dec.)

The ethanolic solution of the dye is almost colourless that turns into pink on adding a drop of an alkali. With 2% caustic soda solution, it gives dark pink colour. The purity of the dye was tested by paper chromatography adopting technique 1A.1B.

Paper used	Whatman No 1
Mobile phase	Butanol saturated with ammonia
Developing agent	1% aqueous caustic soda
Reference dye	Phenolphthalein
Found R_f (Phenolphthalein):	0.93
R_f 5-chloro-2methylphenyl phenol nitro phthal-as-ein:	0.94
Reported R_f (Phenolphthalein)	0.92

Anal. For.: $C_{24}H_{15}NO_5$ (Mol. Wt. 397)

Calc. : C, 72.54; H, 3.78; N, 3.53

Found : C, 72.54; H, 3.78; N, 3.52

3.10.2 PREPARATION OF α -NAPHTHYL CATECHOL NITRO PHTHAL-AS-

EIN:

The dye was prepared by heating a mixture of 1.5g of the acid and 1.0g of catechol in an oil bath at 110 °C to make it uniform and homogeneous. Then the intimate mixture was condensed for about four hours in presence 4-5 drops of concentrated sulphuric acid. The isolation and the purification of the dye were done in a manner similar to that in the case of α -naphthyl phenol phthal-as-ein described in subsection 3.10.1. Yield 1.2g. m.p. >300 °C.

The black dye yields light brown colour in ethanol that intensifies on adding a drop of an alkali.

Anal. For.: $C_{24}H_{15}NO_6$ (Mol. Wt. 413)

Calc. : C, 69.73; H, 3.63; N, 3.39

Found : C, 69.70; H, 3.61; N, 3.36

3.10.3 PREPARATION OF α -NAPHTHYL RESORCINOL NITRO PHTHAL-

AS-EIN:

It was prepared by the condensation of 4.0g of the acid and 2.5g of resorcinol on an oil bath in presence of 8-10 drops of concentrated sulphuric acid at 120-13°C for about four hours. when a brittle mass was obtained on cooling. The brown solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the yellowish orange (green fluorescence) coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 3.3g. m.p. 284-285°C.

The dark red dye dissolves in ethanol giving a yellow colour which becomes yellowish orange with green fluorescence on adding a drop of an alkali. The green fluorescence becomes more intense on addition of 2% caustic soda solution.

Anal. For.: $C_{24}H_{15}NO_6$ (Mol. Wt. 413)

Calc. : C, 69.73; H, 3.63; N, 3.39

Found : C, 69.70; H, 3.60; N, 3.37

3.10.4 PREPARATION OF α -NAPHTHYL HYDROQUINONE NITRO

PHTHAL-AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 170-190 °C for four hours in presence of a few drops of concentrated sulphuric acid. The isolation and purification of the dye was carried out in a manner similar to the one adopted for α -naphthyl resorcinol phthal-as-ein described earlier in subsection 3.10.3 of the chapter. Yield 1.25g.

The black dye, decomposing above 148-150 °C is soluble in ethanol giving a brown colour that turns into light violet on the addition of a drop of an alkali. This colour remains unchanged on addition of 2% caustic potash solution.

Anal. For.: $C_{24}H_{15}NO_6$ (Mol. Wt. 413)

Calc. : C, 69.73; H, 3.63; N, 3.39

Found : C, 69.70; H, 3.59; N, 3.35

3.10.5 PREPARATION OF α -NAPHTHYL PYROGALLOL NITRO PHTHAL-AS-EIN:

The mixture of 1.5g of the acid and 1.0g of pyrogallol was condensed together in presence of 4-5 drops of concentrated sulphuric acid on an oil bath at 130-140 °C for about six hours. The procedure adopted for isolation and purification of the dye was similar to the one adopted for α -naphthyl resorcinol nitro phthal-as-ein described earlier. Yield 1.0g.

The black coloured crystalline dye having m.p. 188-190 °C has an ethanolic solution which is reddish brown in colour and on adding a drop of an alkali becomes violet. Strong basic medium also exhibits the blue black colour.

Anal. For. : $C_{24}H_{15}NO_7$ (Mol. Wt. 429)

Calc. : C, 67.13; H, 3.50; N, 3.26

Found : C, 67.06; H, 3.48; N, 3.22

3.10.6 PREPARATION OF α -NAPHTHYL PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.2g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 210-220 °C for about four hours. The isolation and purification of the dye was performed in the same way as that described for α -naphthyl phenol nitro phthal-as-ein described in subsection 3.10.1 early in this chapter. Yield 1.5g.

The dark brown dye decomposes at 260 °C and yields a light brown colour solution in ethanol that turns brown on adding a drop of an alkali. The colour remains the same in strong basic medium.

Anal. For. : $C_{24}H_{15}NO_7$ (Mol. Wt. 429)

Calc. : C, 67.13; H, 3.50; N, 3.26

Found : C, 67.06; H, 3.47; N, 3.24

3.10.7 ACETYLATION OF α -NAPHTHYL RESORCINOL NITRO PHTHAL-

AS-EIN:

[(α -NAPHTHYL DIACETYL RESORCINOL NITRO PHTHAL -AS-EIN]

1.0g of the α -naphthyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 130-140 °C for about three and half-hours. The hot contents were then poured slowly into a beaker containing a flush of ice and water with constant stirring. It was left overnight whereupon a yellow solid was found settled down. It was filtered, washed well and dried. The crude product was treated with animal charcoal and recrystallised from ethanol mixed with a little acetic acid. It was dried in an oven at 80 °C and then over phosphorous pentaoxide under reduced pressure. Yield 0.70g.

The pale yellow coloured diacetyl derivative is microcrystalline in nature .m.p. 280 °C. It is soluble in acetone, ethanol and acetic acid.

Anal. For. : $C_{28}H_{19}NO_8$ or $C_{24}H_{13}NO_6(OC.CH_3)_2$ (Mol. Wt. 497)

Calc. : C, 67.61; H, 3.82; N, 2.82; acetyl, 17.30

Found : C, 67.55; H, 3.78; N, 2.80; acetyl, 17.25

3.10.8 BROMINATION OF α -NAPHTHYL RESORCINOL NITRO PHTHAL-

AS-EIN:

[(α -NAPHTHYL) DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

The 1.0-g of the dye α -naphthyl resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid. 10% solution of bromine in glacial acetic acid was gradually added in the solution of the dye. The flask was fitted with an air condenser and the contents were refluxed at 120-125 °C for about an hour. The contents were cooled and diluted with minimum quantity of distilled water. A

brownish red powder settled down. It was filtered and washed with water containing acetic acid and finally with hot water for the removal of excess of bromine. It was dissolved in aqueous caustic soda and filtered. The filtrate gave the bromo derivative of the dye on gradual addition of dilute hydrochloric acid. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110 °C in an oven and then in a vacuum dessicator. Yield 0.90g.

The reddish orange crystalline dye having m.p. 280-282 °C is soluble in ethanol giving yellowish orange solution, which turns into yellowish orange with green fluorescence on addition of an alkali.

Anal. For.: $C_{24}H_{13}NBr_2O_6$ (Mol. Wt. 571)

Calc. : Br, 28.02

Found : Br, 27.98

3.10.9 CAUSTIC POTASH TREATMENT OF α -NAPHTHYL RESORCINOL

NITRO PHTHAL-AS-EIN:

5.0g of Potassium hydroxide pellets were placed in a crucible and heated with a few drops of water to turn them into a paste. 1.0g of the dye was then added to the crucible and the contents were heated for about four and half hours till the dark colour of the dye faded completely. After cooling, the contents were diluted with 50ml of water and filtered. A dark red residue (I) settled down on just neutralising the alkali. It was filtered and washed with water. The filtrate when acidified further by adding dilute hydrochloric acid gave a white precipitate (II), which was filtered and washed with water. It was recrystallised from aqueous ethanol and dried in a vacuum dessicator. The filtrate was shaken with ether and on evaporation of the excess of the solvent, a brownish red residue (III) was obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

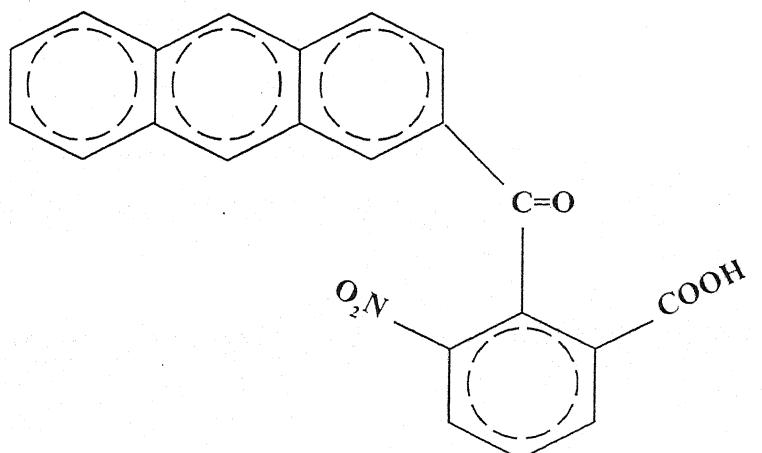
It was recrystallised from acetone. The compound, m. p. 180 °C (dec.), gives

positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(α -naphthoyl)-3-nitro-benzoic by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

The purified residue melted at 109-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart D.

3.11 DYES DERIVED FROM 2-(2'-ANTHRACENOYL)- 3-NITRO BENZOIC**ACID:**

2-(2'-anthracenoyl)-3-nitrobenzoic acid

Figure 3.21

3.11A PREPARATION OF 2-(2'-ANTHRACENOYL)- 3-NITRO BENZOIC ACID:

The acid was prepared in the same way as 2-(α -naphthoyl)-3-nitro benzoic acid. Friedel Crafts reaction was carried out starting with 18g of anthracene (0.1 mole) and 15g of resublimed 3-nitro phthalic anhydride (0.1 mole) in presence of 28g of anhydrous AlCl_3 (0.2 mole). Freshly distilled dried nitrobenzene (AR, 400ml) was used as a solvent.

The acid was isolated as yellowish white crystals, which had a melting point of 158-160°C. The crystalline solid was found to be soluble in hot water, ethanol and methanol. Yield 55%. The acid when fused with caustic potash yielded anthracene-2-carboxylic acid (m.p.279-281°C) along with benzoic acid.

Anal. For.: $\text{C}_{22}\text{H}_{13}\text{NO}_5$ (Mol. Wt. = 371)

Calc. : C, 71.16; H, 3.50; N, 3.77

Found : C, 71.08; H, 3.48; N, 3.72

3.11B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

1.0 g of the acid 3.0 g of fused sodium acetate was refluxed with 15 ml of

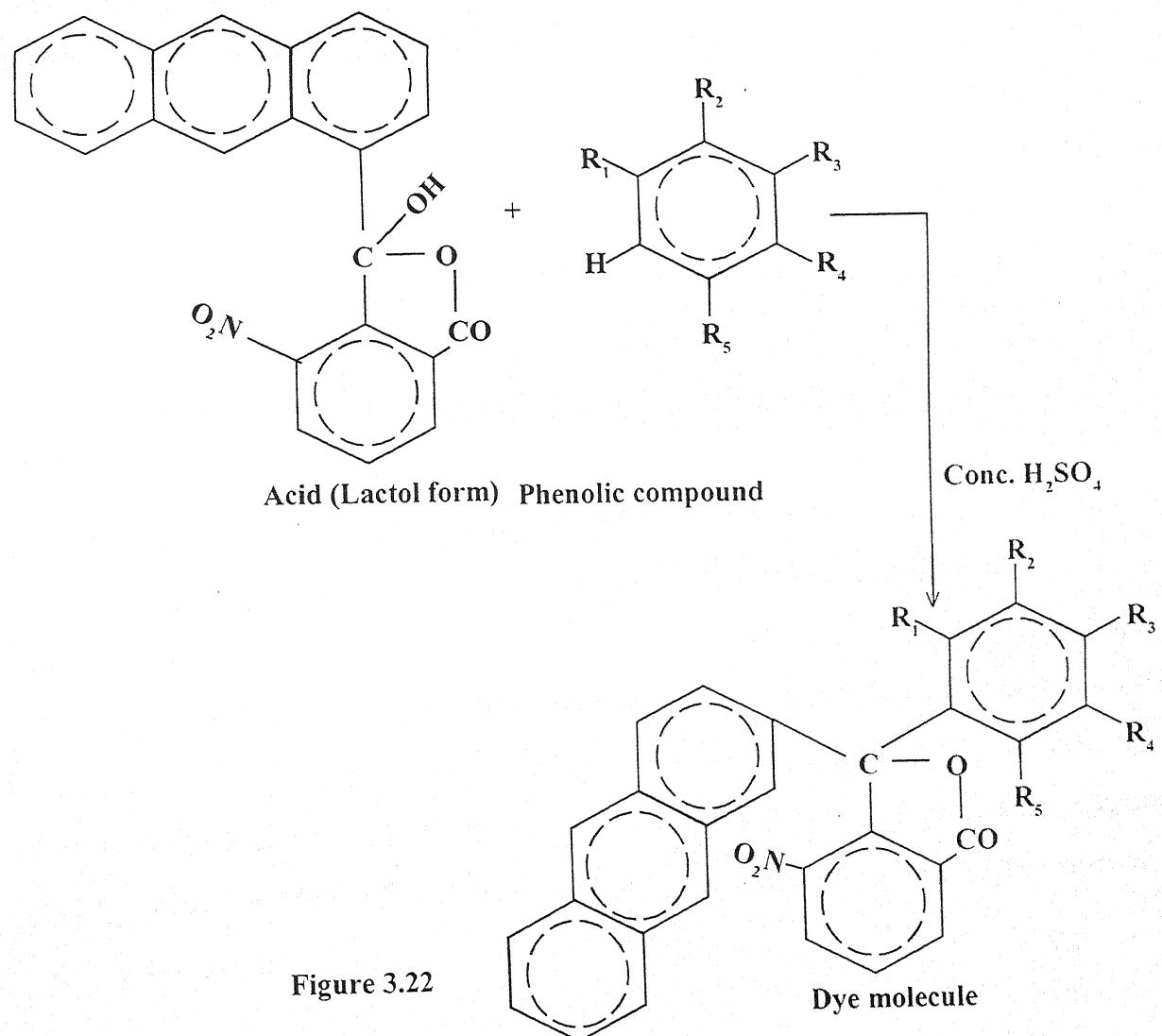
freshly distilled acetic anhydride were used to prepare the derivative as in the case of acetyl derivative of 2-(a-naphthoyl)-3-nitro benzoic acid as described in subsection 3.10B. It was crystallised from acetone in the form of a yellow amorphous solid, m.p.177-179 °C. It is soluble in chloroform, acetone, ethanol and acetic acid. Yield 0.80 g.

Anal. For.: $C_{22}H_{12}NO_5$ (OC.CH₃) (Mol. Wt. = 413)

Calc. : C, 69.73; H, 3.63; N, 3.39; 3; acetyl. 10.41

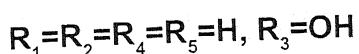
Found : C, 69.65; H, 3.62; N, 3.35; 3; acetyl. 10.38

The dyes prepared from the acid may be represented by the following structures:

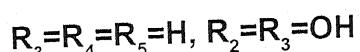


DYES:

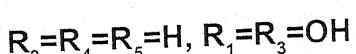
3.11.1 2-anthracyl phenol nitro phthal-as-ein



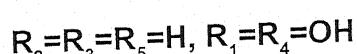
3.11.2 2-anthracyl catechol nitro phthal-as-ein:



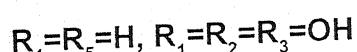
3.11.3 2-anthracyl resorcinol nitro phthal-as-ein:



3.11.4 2-anthracyl hydroquinone nitro phthal-as-ein:



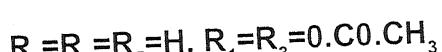
3.11.5 2-anthracyl pyrogallol nitro phthal-as-ein:



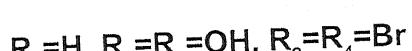
3.11.6 2-anthracyl phloroglucinol nitro phthal-as-ein:



3.11.7 2-anthracyl diacetyl resorcinol nitro phthal-as-ein:



3.11.8 2-anthracyl dibromo resorcinol nitro phthal-as-ein:



3.11.1 PREPARATION OF 2-ANTHRACYL PHENOL NITRO PHTHAL-AS-EIN:

Its preparation, isolation and purification was carried out exactly in the same manner as in the case of α -naphthyl phenol nitro phthal-as-ein as described in subsection 3.10.1. Yield 55%.

The brown coloured crystalline dye has a m.p. 230°C (dec.). The ethanolic solution of the dye is light brown in colour that turns into light pink colour on adding a drop of an alkali. Pink colour imparted by the dye darkens in strong basic medium. The purity of the dye was tested as done in the case of other phenol dyes described in earlier pages.

Anal. For.: $C_{28}H_{17}NO_5$ (Mol. Wt. 447)

Calc. : C, 75.17; H, 3.80; N, 3.13 ;

Found : C, 75.10; H, 3.78; N, 3.10 ;

3.11.2 PREPARATION OF 2-ANTHRACENYL CATECHOL NITRO PHTHAL-

AS-EIN:

Its preparation, isolation and purification was carried out exactly in the same manner as in the case of α -naphthyl catechol nitro phthal-as-ein as described in subsection 3.10.2 except that the condensation was carried out at 140-150 °C. Yield 55%.

The black dye having a m.p. >300 °C is soluble in ethanol to yield a brown colour in ethanol that turns to dark green with alcoholic caustic soda solution.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N, 3.02

Found : C, 72.46; H, 3.65; N, 3.01

3.11.3 PREPARATION OF 2-ANTHRACENYL RESORCINOL NITRO

PHTHAL-AS-EIN:

It was prepared, isolated and purified as described for α -naphthyl resorcinol phthal-as-ein earlier in subsection 3.10.3 earlier in the chapter. Yield 60%.

The red microcrystalline dye having a m.p. >300 °C. It dissolves in ethanol giving a yellow colour which with an alkali turns yellowish orange with green fluorescence in moderate and strong alkaline medium.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N, 3.02

Found : C, 72.48; H, 3.64; N, 3.01

3.11.4 PREPARATION OF 2-ANTHRACENYL HYDROQUINONE NITRO

PHTHAL-AS-EIN:

The preparation, isolation and purification of the dye was carried out in a manner

similar to the one adopted for α -naphthyl resorcinol phthal-as-ein earlier in subsection 3.10.3 earlier in the chapter Yield 65%.

The shining black dye, having m.p. 116-118°C is soluble in ethanol giving a light yellow colour that turns into light pink in moderate and strong basic medium.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N, 3.02

Found : C, 72.50; H, 3.66; N, 3.00

3.11.5 PREPARATION OF 2-ANTHRACENYL PYROGALLOL NITRO

PHTHAL-AS-EIN:

The dye was prepared and purified in a manner identical to the one adopted for α -naphthyl resorcinol phthal-as-ein described in an earlier subsection 3.10.3 Yield 55%.

The black coloured dye having m.p. 260 °C (dec.) gives an ethanolic solution reddish brown in colour which on adding a drop of an alkali becomes violet shade.

Anal. For.: $C_{28}H_{17}NO_7$ (Mol. Wt. 479)

Calc. : C, 70.15; H, 3.55; N, 2.92

Found : C, 70.10; H, 3.52; N, 2.90

3.11.6 PREPARATION OF 2-ANTHRACENYL PHLOROGLUCINOL NITRO

PHTHAL-AS-EIN:

The preparation, isolation and purification of the dye was performed in the same way as that described for the phloroglucinol derivative of 2-(α -naphthoyl)-3-nitro benzoic acid early in this chapter in subsection 3.10.6. Yield 65%.

The dark brown coloured dye has a m.p of. >300°C. It yields a brownish red coloured solution in ethanol that turns red in moderate basic medium. It has deep red colour in strong basic medium.

Anal. For.: $C_{28}H_{17}NO_7$ (Mol. Wt. 479) Calc. : C, 70.15; H, 3.55; N, 2.92

Found : C, 70.10; H, 3.54; N, 2.88

3.11.7

ACETYLATION OF 2-ANTHRACENYL RESORCINOL NITRO

PHTHAL-AS-EIN:

[2-ANTHRACENYL DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN]

1.0g of the 2-anthracenyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were used for undertaking acetylation and the isolation and purification of acetylated product was carried out in exactly the same manner as described in subsection 3.10.7. Yield 0.90g. The light yellow coloured diacetyl derivative (m.p. 214-216 °C) is microcrystalline in nature and is soluble in acetone, ethanol and alkali giving reddish green fluorescence.

Anal. For.: $C_{28}H_{15}NO_6(COCH_3)_2$ (Mol. Wt. 547)

Calc. : C, 70.20; H, 3.84; N, 2.56; acetyl, 15.72

Found : C, 70.12; H, 3.82; N, 2.53; acetyl, 15.69

3.11.8 BROMINATION OF 2-ANTHRACENYL RESORCINOL NITRO

PHTHAL-AS-EIN:

[2-ANTHRACENYL DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

Starting with 1.0-g of the dye the preparation and purification of the dibromo derivative was carried as in the case of α -naphthyl diacetyl resorcinol nitro phthal-as-ein as described in subsection 3.10.8. Yield 0.80g.

The brick red coloured crystalline dye having m.p. 215 °C (dec.) is soluble in ethanol yielding a yellow colour which turns into orange red with green fluorescence on adding an alkali. In strong alkaline medium, it exhibits deep red colour.

Anal. For.: $C_{28}H_{15}NBr_2O_6$ (Mol. Wt. 621)

Calc. : Br, 25.76

Found : Br, 25.65

3.11.9 CAUSTIC POTASH TREATMENT OF 2-ANTHRACENYL

RESORCINOL NITRO PHTHAL-AS-EIN:

1.0g of the dye was used to carry out the caustic potash treatment exactly in the same way as described in subsection 3.10.9 for α -naphthyl resorcinol nitro phthal-

as-ein:

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

It was recrystallised from ethanol m.p.158-160°C. It gives positive tests for carboxyl group and was identified and confirmed as 2-(2'-anthracenoyl) -3-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.

Identification of residue III:

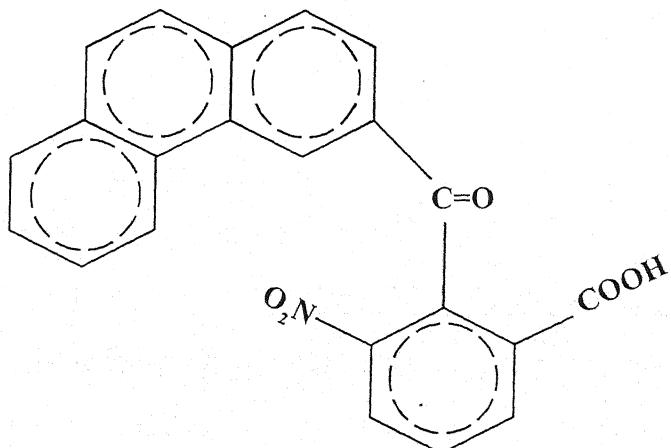
The purified residue melted at 108-110 °C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart D

D.3

3.12 DYES DERIVED FROM 2-(3'-PHENANTHROYL) -3-NITRO - BENZOIC ACID:



2-(3'-phenanthroyl)-3-nitrobenzoic acid

Figure 3.23

3.12A PREPARATION OF 2-(3'-PHENANTHROYL) -3-NITRO - BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between phenanthrene (dry AR, 18g, 0.1mole) and resublimed 3-nitro phthalic anhydride (15.0 g, about 0.1 mole) and anhydrous AlCl_3 (28.0g, about 0.2 moles) was used as a catalyst. Freshly distilled dried nitrobenzene (AR, 200ml) was used as a solvent. The reaction was carried out in a one litre three necked flask fitted with a mechanical stirrer and a condenser connected with a gas absorption trap to remove hydrogen chloride. The flask was warmed a little to dissolve the anhydride and phenanthrene. After cooling the flask to about 0°C , the stirrer was started and AlCl_3 was added in installments. When the vigorous reaction subsided without allowing the temperature to rise above 25°C , the mixture was heated on boiling water at about 90°C on a water bath until evaporation of HCl ceased.

The heavy dark brown coloured complex was decomposed by the addition of 40ml concentrated hydrochloric acid in 250ml-ice cold water. The excess of nitrobenzene was removed by steam distillation. The residue was extracted three four times with boiling 10 % solution of sodium carbonate and filtered. The acid

was precipitated from the filtrate by the gradual addition of concentrated sulphuric acid. It was filtered off, washed well with cold water, dried at 100 °C and recrystallised from aqueous ethanol. It had a melting point of 123-125 °C. The yellowish white prism like crystals were found to be soluble in hot water and ethanol.

Anal. For.: $C_{22}H_{13}NO_5$ (Mol. Wt. = 371)

Calc. : C, 71.16; H, 3.50; N, 3.77;

Found : C, 71.09; H, 3.48; N, 3.75;

3.12B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acetyl derivative of the acid was prepared and purified exactly in the manner the acetyl derivative of 2- α -naphthoyl-3-nitro benzoic acid as described in subsection 3.10B. It is a light brown solid, m.p. 107-109 °C. It is soluble in acetone, chloroform, ethanol and acetic acid.

Anal. For.: $C_{22}H_{12}NO_5(OC.CH_3)$ (Mol. Wt. = 413)

Calc. : C, 69.73; H, 3.63; N, 3.39; acetyl., 10.41

Found : C, 69.62; H, 3.60; N, 3.35; acetyl., 10.38

The dyes prepared from the acid may be represented by the following structures:

PLEASE TURN OVER

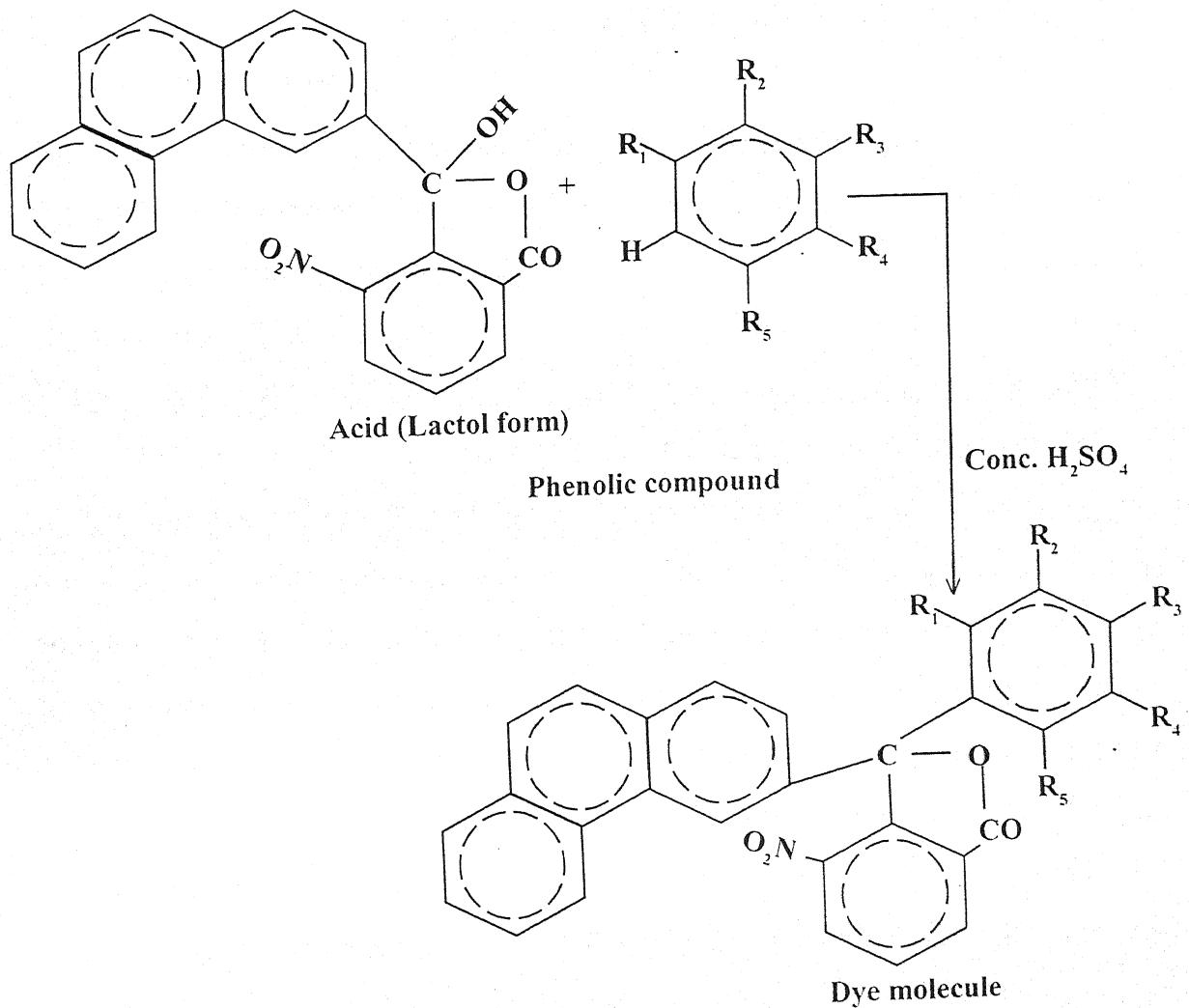
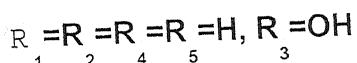


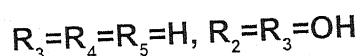
Figure 3.24

DYES:

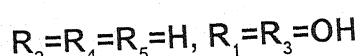
3.12.1 3-phenanthryl phenol nitro phthal-as-ein:



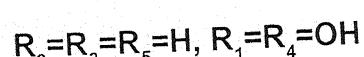
3.12.2 3-phenanthryl catechol nitro phthal-as-ein:



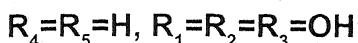
3.12.3 3-phenanthryl resorcinol nitro phthal-as-ein:



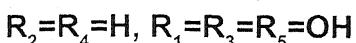
3.12.4 3-phenanthryl hydroquinone nitro phthal-as-ein:



3.12.5 3-phenanthryl pyrogallol nitro phthal-as-ein:



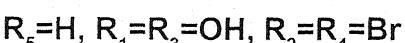
3.12.6 3-phenanthryl phloroglucinol nitro phthal-as-ein:



3.8.7 3-phenanthryl diacetyl resorcinol nitro phthal-as-ein:



3.12.8 3-phenanthryl dibromo resorcinol nitro phthal-as-ein:



3.12.1 PREPARATION OF 3-PHENANTHRYL PHENOL NITRO PHTHAL-AS-EIN:

The dye was prepared starting from a homogenized intimate mixture of 1.5 g of the acid and 1.0 g of phenol (slight excess than molecular proportion) in a hard boiling tube, heating it for some time to make it homogeneous and then condensing in an oil bath in presence of 5-6 drops of concentrated sulphuric acid at 150-170 °C for about six hours when a brittle mass was obtained on cooling. Steam distillation was employed to remove excess of phenol present in the reaction mixture. The brown solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the pinkish red extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 1.30g. m.p. 128-130 °C.

The ethanolic solution of the dye is light yellow coloured that turns into rose pink on adding a drop of an alkali. In strong basic solution, it gives pinkish red colour.

The purity of the dye was tested by paper chromatography adopting technique 1A.1B.

Paper used	Whatman No 1
Mobile phase	Butanol saturated with ammonia
Developing agent	1% aqueous caustic soda
Reference dye	Phenolphthalein
Found R_f (Phenolphthalein):	0.93
R_f (3-phenanthryl) phenol nitro phthal-as-ein :	0.95

Reported R_f (Phenolphthalein) 0.92

Anal. For.: $C_{28}H_{17}NO_5$ (Mol. Wt. 447)

Calc. : C, 75.17; H, 3.80; N, 3.13

Found : C, 75.08; H, 3.78; N, 3.10

3.12.2 PREPARATION OF 3-PHENANTHRYL CATECHOL NITRO PHTHAL-AS-EIN:

The dye was prepared by heating a mixture of 1.5g of the acid and 1.0g of catechol in an oil bath at 120-130 °C about three hours in presence 4-5 drops of concentrated sulphuric acid till the melt became hard. The isolation and the purification of the dye were done in a manner similar to that in the case of α -naphthyl phenol nitro phthal-as-ein described in subsection 3.10.1. Yield 1.2g. m.p. >300 °C.

The black amorphous dye yields blackish green colour in ethanol that intensifies on adding of an alkali.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N, 3.02

Found : C, 72.48; H, 3.65; N, 3.00

3.12.3 PREPARATION OF 3-PHENANTHRYL RESORCINOL NITRO PHTHAL-AS-EIN:

It was prepared by the condensation of 4.0g of the acid and 2.0g of resorcinol on an oil bath in presence of 6-8 drops of concentrated sulphuric acid at 140-150 °C for about four hours. when a hard brittle mass was obtained on cooling. Water was used to remove excess of resorcinol present in the reaction mixture. The brown solid mass left in the flask was extracted with a 2% solution of sodium hydroxide. It was filtered and the dye was precipitated from the yellowish orange (green fluorescence) coloured extract by the gradual addition of dilute hydrochloric acid with constant stirring. It was purified by repeated crystallisation from rectified spirit and dried in vacuum in a dessicator. Yield 2.8g. m.p. 319-321 °C. The microcrystalline red dye dissolves in ethanol giving a yellow colour which becomes yellowish orange with green fluorescence on adding a drop of an alkali.

The green fluorescence becomes more intense on addition of strong basic solution.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N,

Found : C, 72.48; H, 3.69; N,

3.12.4 PREPARATION OF 3-PHENANTHRYL HYDROQUINONE NITRO PHTHAL-

AS-EIN:

1.5g of the acid and 1.0g of hydroquinone were mixed to form an intimate and homogeneous mixture and treated in an oil bath at 130-140 °C for four hours in presence of a few drops of concentrated sulphuric acid when the molten mass became hard and brittle on cooling. The isolation and purification of the dye was carried out in a manner similar to the one adopted for α -naphthyl resorcinol nitro phthal-as-ein described earlier in subsection 3.10.3 of the chapter. Yield 1.2g.

The brown microcrystalline dye has a m.p. 87-89 °C and is soluble in ethanol giving a light brown colour that turns into greenish brown on the addition of a drop of an alkali. This colour remains unchanged on addition of strong potash solution.

Anal. For.: $C_{28}H_{17}NO_6$ (Mol. Wt. 463)

Calc. : C, 72.57; H, 3.67; N, 3.02

Found : C, 72.50; H, 3.66; N, 2.99

3.12.5 PREPARATION OF 3-PHENANTHRYL PYROGALLOL NITRO PHTHAL-AS-

EIN:

It was prepared following exactly the same procedure as described for α -naphthyl resorcinol nitro phthal-as-ein described earlier. Yield 1.6g.

The dark crystalline dye having m.p. above 300 °C has an ethanolic solution which is brownish red in colour and in a moderate alkali it becomes violet. Strong basic medium also exhibits the blue violet colour.

Anal. For.: $C_{28}H_{17}NO_7$ (Mol. Wt. 479)

Calc. : C, 70.15; H, 3.55; N, 2.92

Found : C, 70.10; H, 3.54; N, 2.90

3.12.6 PREPARATION OF 3-PHENANTHRYL PHL0ROGLUCINOL NITRO

PHTHAL-AS-EIN:

The intimate and thoroughly homogeneous mixture of 1.5g of the acid and 1.2g of phloroglucinol along with a few drops of concentrated sulphuric acid was together heated on an oil bath at 120 °C for about three and a half hours till the melt became hard and brittle on cooling. The isolation and purification of the dye was performed in the same way as that described for ?-naphthyl phenol nitro phthal-as-ein described in subsection 3.10.6 early in this chapter. Yield 1.0g.

The orange brown dye has m.p.> 300 °C and yields a reddish brown colour solution in ethanol that turns to red on adding a drop of an alkali. The colour becomes deep red in strong basic medium.

Anal. For. : C₂₈H₁₇NO₇ (Mol. Wt. 479)

Calc. : C, 70.15; H, 3.55; N, 2.90

Found : C, 70.08; H, 3.53; N, 2.88

3.12.7 ACETYLATION OF 3-PHENANTHRYL RESORCINOL NITRO PHTHAL-AS-

EIN:

[3-PHENANTHRYL DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN]

1.0g of the 3-phenanthryl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were taken in a 50ml round bottom flask fitted with an air condenser. The contents were refluxed at 130-140 °C for about three and half hours. The hot contents were then poured slowly into a beaker containing a slush of ice and water with constant stirring. It was left overnight whereupon a yellow solid was found settled down. It was filtered, washed well and dried. The crude product yellow in colour was treated with animal charcoal and recrystallised from acetone. It was dried in an oven and then over phosphorous pentaoxide under reduced pressure. Yield 0.80g.

The amorphous yellow coloured diacetyl derivative melts at 196-198 °C. It is soluble in acetone, ethanol and acetic acid. Its ehanolic solution is yellow coloured which turns into reddish green fluorescence in moderate alkaline medium and deep red in strong basic medium.

Anal. For.: $C_{28}H_{15}NO_6(OCH_3)_2$ (Mol. Wt. 547)

Calc. : C, 70.20; H, 3.84; N, 2.56; acetyl, 15.72

Found : C, 70.10; H, 3.82; N, 2.52; acetyl, 15.69

3.12.8 BROMINATION OF 3-PHENANTHRYL RESORCINOL NITRO PHTHAL-AS-

EIN:

[(3-PHENANTHRYL) DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

The 1.0-g of the dye 3-phenanthryl resorcinol nitro phthal-as-ein was dissolved in minimum quantity of glacial acetic acid and prepared in the same way as α -naphthyl resorcinol nitro phthal-as-ein. The crude bromo derivative of the dye was finally purified with aqueous ethanol and dried at 110 °C in an oven and then in a vacuum dessicator. Yield 0.80g.

The brick red microcrystalline dye having m.p. 150-152 °C is soluble in ethanol, acetone and acetic acid. It dissolves in ethanol giving yellowish red solution, which turns into yellowish orange with green fluorescence on addition of a moderate or strong alkali.

Anal. For.: $C_{28}H_{15}NBr_2O_6$ (Mol. Wt. 621)

Calc. : Br, 25.76

Found : Br, 25.72

3.12.9 CAUSTIC POTASH TREATMENT OF 3-PHENANTHRYL RESORCINOL

NITRO PHTHAL-AS-EIN:

1.0g of the dye was subjected to caustic potash treatment in a manner almost identical to that followed for α -naphthyl resorcinol nitro phthal-as-ein. The following three residues were obtained:

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the resorcinol dye.

Identification of the residue II:

It was recrystallised from aqueous ethanol. The compound, m. p. 123-125°C gives positive tests for carboxyl and phenolic groups and was identified and confirmed as 2-(3'-phenanthroyl) -3-nitro-benzoic by mixed melting point determination and superimposition of IR spectra on that of the authentic sample.

Identification of residue III:

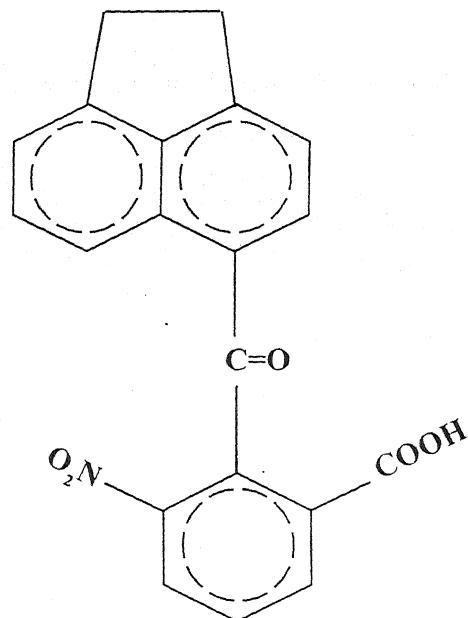
The purified residue melted at 109-110°C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in Chart D

D.4

3.13DYES DERIVED FROM 2-(3'-ACENAPHTHOYL)- 3-NITRO BENZOIC

ACID:



2-(3'-acenaphthoyl)-3-nitrobenzoic acid

Figure 3.25

3.13A PREPARATION OF 2-(3'-ACENAPHTHOYL)- 3-NITRO BENZOIC ACID:

The acid was prepared by carrying out Friedel Crafts reaction between acenaphthene and 3-nitro phthalic anhydride in presence of anhydrous aluminium chloride. The acid was recrystallised from aqueous ethanol in the form of colourless needle m.p. 199-201 °C.

The crystalline solid was found to be soluble in ethanol ether, chloroform and sparingly soluble in benzene and insoluble in carbondisulphide.

Anal. For. : C₂₀H₁₃NO₅ (Mol. Wt. = 347)

Calc. : C, 69.16; H, 3.75; N, 4.03

Found : C, 69.04; H, 3.74; N, 4.00

3.13B PREPARATION OF ACETYL DERIVATIVE OF THE ACID:

The acetyl derivative of 2-(3'-acenaphthoyl)-3-nitro benzoic acid was prepared

in the same way as the acetyl derivative of 2-(α -naphthoyl)-3-nitro-benzoic acid as described in subsection 3.10B. It has a m.p. of m.p. 174-175 °C. It is soluble in chloroform, ethanol and acetic acid. Yield 0.75 g.

Anal. For.: $C_{20}H_{12}NO_5$ (OC₂H₅) (Mol. Wt. = 389)

Calc. : C, 67.87; H, 3.86; N, 3.60; acetyl, 11.05

Found : C, 67.70; H, 3.85; N, 3.55; acetyl, 11.02

The dyes prepared from the acid may be represented by the following structures:

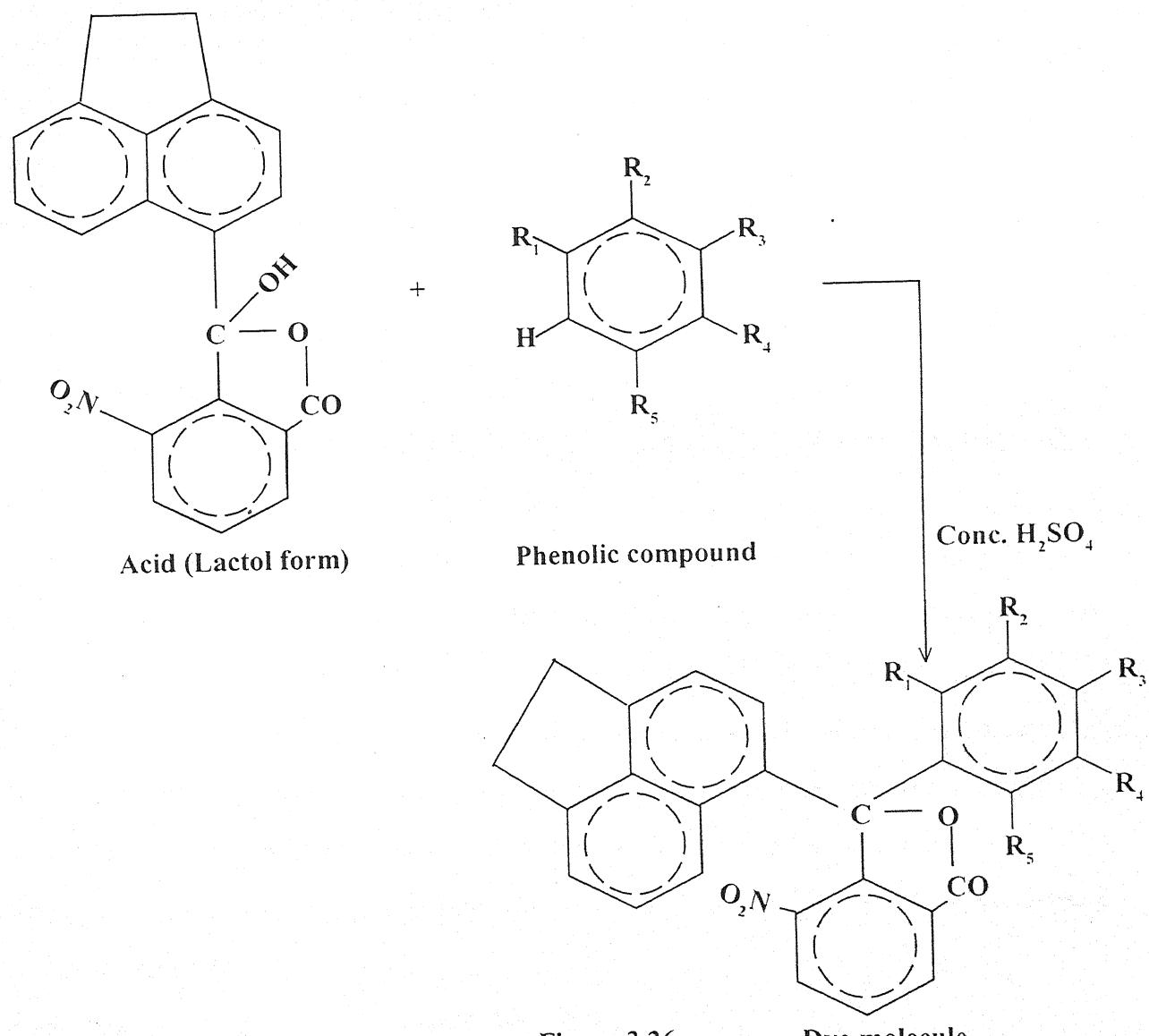
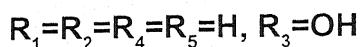


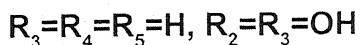
Figure 3.26

DYES:

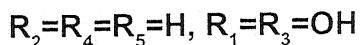
3.13.1 3-acenaphthyl phenol nitro phthal-as-ein:



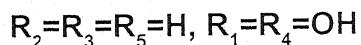
3.13.2 3-acenaphthyl catechol nitro phthal-as-ein:



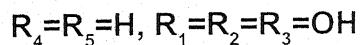
3.13.3 3-acenaphthyl resorcinol nitro phthal-as-ein:



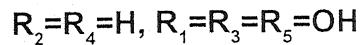
3.13.4 3-acenaphthyl hydroquinone nitro phthal-as-ein:



3.13.5 3-acenaphthyl pyrogallol nitro phthal-as-ein:



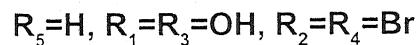
3.13.6 3-acenaphthyl phloroglucinol nitro phthal-as-ein:



3.13.7 3-acenaphthyl diacetyl resorcinol nitro phthal-as-ein:



3.13.8 3-acenaphthyl dibromo resorcinol nitro phthal-as-ein:



3.13.1 PREPARATION OF 3-ACENAPHTHYL NITRO PHENOL PHTHAL-AS-

EIN:

Starting from 1.5g of the acid and 1.0g of phenol its preparation, isolation and purification was carried out exactly in the same manner as in the case of α -naphthyl phenol nitro phthal-as-ein as described in subsection 3.10.1. Yield 1.2g.

The grey coloured crystalline dye has a m.p. 110-112 °C. The ethanolic solution of the dye is light yellow in colour that turns into pink colour on adding a drop of an alkali. Pink colour imparted by the dye darkens in strong basic medium.

The purity of the dye was tested as done in the case of other phenol dyes described in earlier pages.

Anal. For.: $C_{26}H_{17}NO_5$ (Mol. Wt. 423)

Calc. : C, 73.76; H, 4.02; N, 3.31;

Found : C, 73.68; H, 4.00; N, 3.29;

3.13.2 PREPARATION OF 3-ACENAPHTHYL CATECHOL NITRO PHTHAL-AS-EIN:

Its preparation, isolation and purification was carried out exactly in the same manner as in the case of α -naphthyl catechol nitro phthal-as-ein as described in subsection 3.10.2 by condensing 1.5g of the acid and 1.0g of catechol at 130-140 °C. Yield 1.1g.

The dark brown dye having a m.p. >300 °C is soluble in ethanol to yield a brown colour in ethanol that turns to bluish green with alcoholic caustic soda solution.

Anal. For. : $C_{26}H_{17}NO_6$ (Mol. Wt. 439)

Calc. : C, 71.07; H, 3.87; N, 3.19

Found : C, 70.98; H, 3.86; N, 3.14

3.13.3 PREPARATION OF 3-ACENAPHTHYL RESORCINOL NITRO PHTHAL-AS-EIN:

Taking 4.0g of the resorcinol dye and 2.5g of resorcinol it was prepared, isolated and purified as described for α -naphthyl resorcinol nitro phthal-as-ein earlier in subsection 3.10.3. Yield 3.2g.

The red microcrystalline dye having a m.p. 309-311°C. It dissolves in ethanol giving a yellow colour, which with an alkali turns yellowish orange with green fluorescence in moderate and strong basic medium.

Anal. For. : $C_{26}H_{17}NO_6$ (Mol. Wt. 439)

Calc. : C, 71.07; H, 3.87; N, 3.19

Found : C, 70.94; H, 3.85; N, 3.17

3.13.4 PREPARATION OF 3-ACENAPHTHYL HYDROQUINONE NITRO PHTHAL-AS-EIN:

The preparation, isolation and purification of the dye was carried out in a manner

similar to the one adopted for α -naphthyl hydroquinone nitro phthal-as-ein earlier in subsection 3.10.4 earlier in the chapter Starting from 1.5g of the acid and 1.0g of hydroquinone the yield was 0.9g.

The dark brown powdery dye, having m.p. 200-202 °C is soluble in ethanol giving a reddish brown colour that turns into purple in basic medium.

Anal. For.: $C_{26}H_{17}NO_6$ (Mol. Wt. 439)

Calc. : C, 71.07; H, 3.87; N, 3.19

Found : C, 70.98; H, 3.86; N, 3.15

3.13.5 PREPARATION OF 3-ACENAPHTHYL PYROGALLOL NITRO PHTHAL-AS-EIN:

The dye was prepared by condensing 1.5g of the acid and 1.0g of pyrogallol at 180-170 °C for about six hours in presence of 6-8 drops of concentrated sulphuric acid. It was isolated and purified in a manner identical to the one adopted for α -naphthyl pyrogallol nitro phthal-as-ein described in an earlier subsection 3.10.5. Yield 0.90g.

The shining black coloured microcrystalline dye having m.p. 208-210 °C gives an ethanolic solution reddish brown in colour which on adding a drop of an alkali becomes violet. In strong basic medium it exhibits blue black colour.

Anal. For.: $C_{26}H_{17}NO_7$ (Mol. Wt. 455)

Calc. : C, 68.57; H, 3.74; N, 3.08

Found : C, 68.45; H, 3.72; N, 3.05

3.13.6 PREPARATION OF 3-ACENAPHTHYL PHLOROGLUCINOL NITRO PHTHAL-AS-EIN:

Beginning with 1.5g of the acid and 1.5g of phloroglucinol preparation, isolation and purification of the dye was performed in the same way as that described for the phloroglucinol derivative of 2-(α -naphthoyl)-3-nitro benzoic acid early in this chapter in subsection 3.10.6. Yield 1.4g.

The light brown coloured microcrystalline dye has a m.p. of 240 °C (dec.). It yields a brown red coloured solution in ethanol that turns dark brown in basic medium.

Anal. For.: $C_{26}H_{17}NO_7$

(Mol. Wt. 455)

Calc. : C, 68.57; H, 3.74; N, 3.08

Found : C, 68.45; H, 3.72; N, 3.02

3.13.7 ACETYLATION OF 3-ACENAPHTHYL RESORCINOL NITRO PHTHAL-

AS-EIN:

[3-ACENAPHTHYL DIACETYL RESORCINOL NITRO PHTHAL-AS-EIN]

1.0g of the 2-acenaphthyl resorcinol nitro phthal-as-ein dye, 3.0g of fused sodium acetate and 15ml of freshly distilled acetic anhydride were used for undertaking acetylation and the isolation and purification of acetylated product which was carried out in exactly the same manner as described in subsection 3.10.7. Yield 0.90g.

The yellowish white coloured diacetyl derivative (m.p. 148-150 °C) is amorphous nature and is soluble in acetone, ethanol and acetic acid.

Anal. For.: $C_{26}H_{15}NO_6(COCH_3)_2$ (Mol. Wt. 523)

Calc. : C, 68.83; H, 4.01; N, 2.68; acetyl, 16.44

Found : C, 68.72; H, 3.99; N, 2.65; acetyl, 16.41

3.13.8 BROMINATION OF 3-ACENAPHTHYL RESORCINOL NITRO PHTHAL-

AS-EIN:

[3-ACENAPHTHYL DIBROMO RESORCINOL NITRO PHTHAL-AS-EIN]

Starting with 1.0-g of the dye the preparation and purification of the dibromo derivative was carried as in the case of α -naphthyl diacetyl resorcinol nitro phthal-as-ein as described in subsection 3.10.8. Yield 0.80g.

The brick red coloured microcrystalline dye having m.p. 136-138 °C is soluble in ethanol yielding a yellow colour, which turns into yellowish orange with green fluorescence on adding an alkali. In strong alkaline medium, it exhibits deep red colour.

Anal. For. : $C_{26}H_{15}NBr_2O_6$

(Mol. Wt. 597)

Calc. : Br, 26.80

Found : Br, 26.78

3.13.9 CAUSTIC POTASH TREATMENT OF 3-ACENAPHTHYL RESORCINOL NITRO

PHTHAL-AS-EIN:

1.0g of the dye was used to carry out the caustic potash treatment exactly in the same way as described in subsection 3.10.9 for 3-acenaphthyl resorcinol nitro phthal-as-ein. Three residues were obtained.

Identification of residue I:

It was identified and confirmed as the unreacted residual dye from its colour reactions and melting point determination with the authentic sample of the dye.

Identification of the residue II:

This yellowish compound, m.p. 199-201°C gives positive tests for carboxyl group and was identified and confirmed as 2-(3'-acenaphthoyl-3-nitro benzoic acid by mixed melting point determination and superimposition of IR spectra on that of the original sample.

Identification of residue III:

The purified residue melted at 108-110°C. It gave blue violet colour with ferric chloride. It reduced Fehling's solution, ammoniacal silver nitrate and gave fluorescein test with phthalic anhydride. On the basis of these observations, it was confirmed to be resorcinol.

Acetylation, bromination and caustic potash treatment of the dye are depicted in

Chart D

APPENDIX
Colours/shades of dyes

TABLE I
Dyes derived from 2-(2'-hydroxy-5'-methylbenzoyl) benzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol Neutral			λ _{max.} (nm)	pH	Medium
			Alkaline	Pink	--			
Phenol	Pinkish red	182-84	Light yellow	Pink	--	535	8.6	Alkaline
Resorcinol	Dark orange	290-92	Yellow	Golden	470	5.5	Neutral	
Catechol	Black	>360	Brown	Blackish green	510	10.2	Alkaline	
Hydroquinone	Black	>320	Crimson	Dark brown	--	--	Neutral	
Phloroglucinol	Orange	320-22	Yellow	Dark Red	--	480	9.0	Alkaline
Pyrogallol	Black	>360	Wine red	Blue violet	--	--	Neutral	
Diacetyl	Yellow	188-89	Colorless	Yellowish G.F.	--	--	Neutral	
Dibromo	Orange	250-51	Red	Reddish	510	5.8	Neutral	
				Pink G.F.	510	8.7	Alkaline	

TABLE II
Dyes derived from 2-(5'-chloro-2'-methylbenzoyl) benzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol Neutral			λ _{max.} (nm)	pH	Medium
			Alkaline	Pink	--			
Phenol	Buff dye	142-44	Brownish red	Pink	--	530	8.8	Alkaline
Resorcinol	Red	278-79	Golden yellow	Reddish	460	5.6	Neutral	
Catechol	Black	>360	Brown	Yellow G.F.	490	9.0	Alkaline	
Hydroquinone	Black	>300	Golden brown	Brownish black	--	--	Neutral	
Phloroglucinol	Dark orange	>360	Golden yellow	Leaf brown	--	--	Alkaline	
Pyrogallol	Black	>300	Wine red	Reddish Orange	490	9.2	Neutral	
Diacetyl resorcinol dye	Pale yellow	175-76	Yellow	Violet	--	--	Alkaline	
Dibromo resorcinol dye	Pale orange	250-51	Yellowish orange	Yellowish G.F.	--	520	6.0	Neutral
				Reddish orange G.F.	520	9.5	Alkaline	

TABLE III
Dyes derived from 2-(3'-chloro-4'-chloromethylbenzoyl) benzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol				pH	Medium
			Neutral	Alkaline	λ _{max.} (nm)			
Phenol	Dark	113-15	Reddish cream	Pink	--		--	Neutral
	Brown				535		8.6	Alkaline
Resorcinol	Dark red	287-88 dec.	Yellow GF	Brownish RedGF.	460		6.4	Neutral
	Black	>360	Brownish black	Brownish black	490		9.6	Alkaline
Catechol	Black	>360	Brown	Blackish brown	--		--	Neutral
				--	--		--	Alkaline
Hydroquinone	Black	>360 dec.		Dark	--		--	Neutral
				red	500		--	Alkaline
Phloroglucinol	reddish brown	>180	Golden yellow	--			--	Neutral
				Dark red	--		--	Alkaline
Pyrogallol	Black	>315	Wine red	Dark violet	--		--	Neutral
				Yellowish G.F.	--		--	Alkaline
Diacetyl resorcinol dye	Pale yellow	182-84	Almost colourless	--	--		--	Neutral
					--		--	Alkaline
Dibromo resorcinol dye	Dark orange	290-92	Yellow	Yellowish orangeGF:	520		6.0	Neutral
					520		9.5	Alkaline

TABLE IV
Dyes derived from 2-(2'-hydroxy--5'-methylbenzoyl) tetrachlorobenzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol				pH	Medium
			Neutral	Alkaline	λ _{max.} (nm)			
Phenol	Reddish orange	220-22	Light yellow	Violet	510		5.8	Neutral
					535		8.6	Alkaline
Resorcinol	greenish brown	280-81 dec.	Cream	Reddish orange G.F.	470		5.8	Neutral
					520		9.6	Alkaline
Catechol	Black	242-43	Golden brown	Brown	--		--	Neutral
					--		--	Alkaline
Hydroquinone	Black	270-71 dec.	Light brown	Brown	--		--	Neutral
					--		--	Alkaline
Phloroglucinol	Dark red	>180	Wine red	Deep red GF	490		9.8	Alkaline
					--		--	Neutral
Pyrogallol	Black	>360	Dark brown	Blue	--		--	Neutral
					--		--	Alkaline
Triacetyl resorcinol dye	Golden brown	165-67	Almost colourless	Yellowish G.F.	--		--	Neutral
					--		--	Alkaline
Tribromo resorcinol dye	Cream	315-317	Yellowish Orange	Yellowish orangeGF	520		6.0	Neutral
					530		10.4	Alkaline

TABLE V
Dyes derived from 2-(5'-chloro--2'-methylbenzoyl) tetrachlorobenzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol		$\lambda_{\max.}(\text{nm})$	pH	Medium
			Neutral	Alkaline			
Phenol	Orange brown	260-62	Light yellow	Violet	510	5.6	Neutral
Resorcinol	Lemon yellow	299-300	Pale cream	Light orange G.F.	460 510	5.5 9.5	Neutral Alkaline
Catechol	Black	250	Light brown	Golden brown	-- --	-- --	Neutral Alkaline
Hydroquinone	Black	>300	Golden brown	Yellowish brown	-- --	-- --	Neutral Alkaline
Phloroglucinol	Grey	>300	Grey	Pale cream	500	8.5	Neutral Alkaline
Pyrogallol	Black	180 dec.	Light brown	Blackish brown	-- --	-- --	Neutral Alkaline
Diacetyl resorcinol dye	Buff colour	180-82	Pale yellow	Reddish G.F.	-- --	-- --	Neutral Alkaline
Dibromo resorcinol dye	Grey	160-62	Light Pink	Pink	520 GF 530	5.5 9.0	Neutral Alkaline

TABLE VI
Dyes derived from 2-(3'-chloro--4'-chloromethylbenzoyl) tetrachlorobenzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol		$\lambda_{\max.}(\text{nm})$	pH	Medium
			Neutral	Alkaline			
Phenol	Pinkish white	240-42	Light yellow	Rose red	510 530	5.9 9.0	Neutral Alkaline
Resorcinol	Golden yellow	306-08	Deep orange G.F.	Deep red G.F.	455 500	5.6 9.5	Neutral Alkaline
Catechol	Black	260	Brown	Dark brown	-- --	-- --	Neutral Alkaline
Hydroquinone	Black	>360	Leaf brown	Deep brown	-- --	-- --	Neutral Alkaline
Phloroglucinol	blackish brown	>310	Golden brown	Dark red	490	8.5	Neutral Alkaline
Pyrogallol	blackish brown	>360 dec.	Leaf brown	Violet	-- --	-- --	Neutral Alkaline
Diacetyl resorcinol dye	Buff colour	167-69	Light yellow	Pink	-- --	-- --	Neutral Alkaline
Dibromo resorcinol dye	blackish rose	235-37			520 pink GF 530	5.5 10.0	Neutral Alkaline

TABLE VII
Dyes derived from 2-(2'-hydroxy-5'-methylbenzoyl)-3-nitrobenzoic acid

Phenols	Colour of dye	m.p. °C	Neutral	Alkaline	λ _{max.} (nm)	pH	Medium
Phenol	Brown	>360	Light brown	Light pink	530	9.0	Alkaline
Resorcinol	Brown	301-303	Light yellow	Brownish red G.F.	460 500	6.0 9.5	Neutral Alkaline
Catechol	Brownish black	>360	Light brown	Brown	--	--	Neutral
Hydroquinone	Black	262	Light green	Brown	--	--	Alkaline
Phloroglucinol	Red	>360	Wine red	Orange red	495	8.6	Neutral
Pyrogallol	Brownish black	>360	Light brown	Light violet	--	--	Alkaline
Triacetyl resorcinol dye	Deep yellow	242	Yellowish brown	Reddish G.F.	--	--	Neutral
Tribromo resorcinol dye	Brown	174	Pink	Deep pink	520 530	5.5 8.5	Neutral Alkaline

TABLE VIII
Dyes derived from 2-(5'-chloro-2'-methylbenzoyl)-3-nitro benzoic acid

Phenols	Colour of dye	m.p. °C	Neutral	Alkaline	λ _{max.} (nm)	pH	Medium
Phenol	Blackish brown	300	Brown	Reddish violet	550	9.0	Alkaline
Resorcinol	Greenish brown	312	Lemon yellow	Red G.F.	460 510	6.0 9.5	Neutral Alkaline
Catechol	Black	>360	Brown brown	Brownish black	--	--	Neutral
Hydroquinone	Black	234 dec.	Light brown	Dark brown	--	--	Neutral
Phloroglucinol	Brownish red	>320	Orange red	Deep orange red	500	8.5	Alkaline
Pyrogallol	Black	>360 dec.	Light brown	Brown	--	--	Neutral
Diacetyl resorcinol dye	Pale cream	280	Light yellow	Reddish G.F.	--	--	Alkaline
Tribromo resorcinol dye	Dark	182	Pink	Reddish pink GF	520 500	5.5 8.2	Neutral Alkaline

TABLE IX

Dyes derived from 2-(3'-chloro--4'-chloromethylbenzoyl)-3-nitro benzoic acid

Phenols	Colour		Colour in ethanol		$\lambda_{\max.}(\text{nm})$	pH	Medium
	of dye	m.p. °C	Neutral	Alkaline			
Phenol	Light pink	214-16	Light brown	Light violet	550	9.5	Alkaline
Resorcinol	Reddish brown	225-27	Golden yellow	Brown	460	5.8	Neutral
Catechol	Black	250	Light brown	Golden brown	520	8.6	Alkaline
Hydroquinone	Black	314-16	Light brown	Reddish brown	--	--	Neutral
Phloroglucinol	Brown	298-99	Wine red	Dark red	--	--	Neutral
Pyrogallol	Black	342-43	Reddish brown	Reddish brown	510	9.2	Alkaline
Diacetyl resorcinol dye	Leaf brown	264-266	Almost colourless	Pinkish G.F.	--	--	Neutral
Dibromo resorcinol dye	Dark brown	160-62	Yellowish red	Orange GF	530	6.5	Neutral
					530	8.8	Alkaline

TABLE X

Dyes derived from 2- α -naphthoyl-3-nitro benzoic acid

Phenols	Colour		Colour in ethanol		$\lambda_{\max.}(\text{nm})$	pH	Medium
	of dye	m.p. °C	Neutral	Alkaline			
Phenol	Brown	120 dec.	Colourless	Pink	--	--	Neutral
					530	9.6	Alkaline
Resorcinol	Dark red	281-83	Yellow	Yellowish orange G.F.	460	6.4	Neutral
					490	9.8	Alkaline
Catechol	Black	>300	Light brown	Brown	--	--	Neutral
					--	--	Alkaline
Hydroquinone	Black	148-50	Brown	Light violet	--	--	Neutral
					--	--	Alkaline
Phloroglucinol	Dark brown	260 dec.	Light brown	Brown	--	--	Neutral
					490	8.4	Alkaline
Pyrogallol	Black	188-89	Reddish brown	Violet	--	--	Neutral
					--	--	Alkaline
Diacetyl resorcinol dye	Pale yellow	210-12	Almost colourless	Yellowish G.F.	--	--	Neutral
					--	--	Alkaline
Dibromo resorcinol dye	Reddish orange	280-82	Yellowish red	Yellowish orange GF	530	6.0	Neutral
					530	9.0	Alkaline

TABLE XI
Dyes derived from 2-(3'-phenanthroyl)-3- nitro benzoic acid

Phenols	Colour of dye	m.p. °C	Neutral		Alkaline	$\lambda_{\max.}(\text{nm})$	pH	Medium
			Colour in ethanol					
Phenol	Brown	128-30	Light yellow		Rose pink	500 530	6.2 9.0	Neutral Alkaline
Resorcinol	Red	319-21	Yellow		Yellowish orange G.F.	460 500	6.0 8.4	Neutral Alkaline
Catechol	Black	>300	Blackish green		Blackish green	-- --	-- --	Neutral Alkaline
Hydroquinone	Brown	87-89	Light brown		Greenish brown	-- --	-- --	Neutral Alkaline
Phloroglucinol	Orange brown	>300	Reddish brown		Red	-- 500	-- 9.0	Neutral Alkaline
Pyrogallol	Black	>300	Brownish dec. red		Violet	-- --	-- --	Neutral Alkaline
Diacetyl resorcinol dye	Yellow	196-98	Yellow		Reddish G.F.	-- --	-- --	Neutral Alkaline
Dibromo resorcinol dye	Brick red	148-50	Yellowish red		Yellowish orange G.F.	520 520	6.0 8.4	Neutral Alkaline

TABLE XII
Dyes derived from 2-(2'-anthracenoyl)-3-nitro benzoic acid

Phenols	Colour of dye	m.p. °C	Neutral		Alkaline	$\lambda_{\max.}(\text{nm})$	pH	Medium
			Colour in ethanol					
Phenol	Brown	230	Light dec. brown		Light pink	510 530	5.8 9.5	Neutral Alkaline
Resorcinol	Red	>300	Yellow		Yellowish G.F.	460 500	5.6 9.5	Neutral Alkaline
Catechol	Black	>300	Brown		Dark green	-- --	-- --	Neutral Alkaline
Hydroquinone	Black	116-18	Light yellow		Light pink	-- --	-- --	Neutral Alkaline
Phloroglucinol	Dark brown	>300	Brownish red		Red	-- 480	-- 9.0	Neutral Alkaline
Pyrogallol	Black	260	Red		Violet	-- --	-- --	Neutral Alkaline
Diacetyl resorcinol dye	Light yellow	214-16	Light yellow		Reddish G.F.	-- --	-- --	Neutral Alkaline
Dibromo resorcinol dye	Brick red	215	Yellow dec.		Orange:520 red G.F.:530	-- --	6.2 8.5	Neutral Alkaline

TABLE XIII
Dyes derived from 2-(3'-acenaphthoyl)-3-nitro benzoic acid

Phenols	Colour of dye	m.p. °C	Colour in ethanol		λ_{\max} (nm)	pH	Medium
			Neutral	Alkaline			
Phenol	Grey	110-12	Light yellow	Pink	500 530	6.3 8.8	Neutral Alkaline
Resorcinol	Red	309-311	Yellow	Yellowish orange G.F.	455 500	5.8 9.0	Neutral Alkaline
Catechol	Blackish brown	>300	Brown	Bluish green	-- --	-- --	Neutral Alkaline
Hydroquinone	brown brown	200-02	Reddish brown	Purple	-- --	-- --	Neutral Alkaline
Phloroglucinol	Light brown	240 dec.	Light brown	Dark brown	-- 500	-- 8.6	Neutral Alkaline
Pyrogallol	Black	208-10	Reddish brown	Violet	-- --	-- --	Neutral Alkaline
Diacetyl resorcinol dye	Yellowish white	148-50	Light yellow	Yellowish G.F.	-- --	-- --	Neutral Alkaline
Dibromo resorcinol dye	Brick red	136-38	Yellow	Yellowish orange G.F.	530 530	5.5 9.5	Neutral Alkaline

